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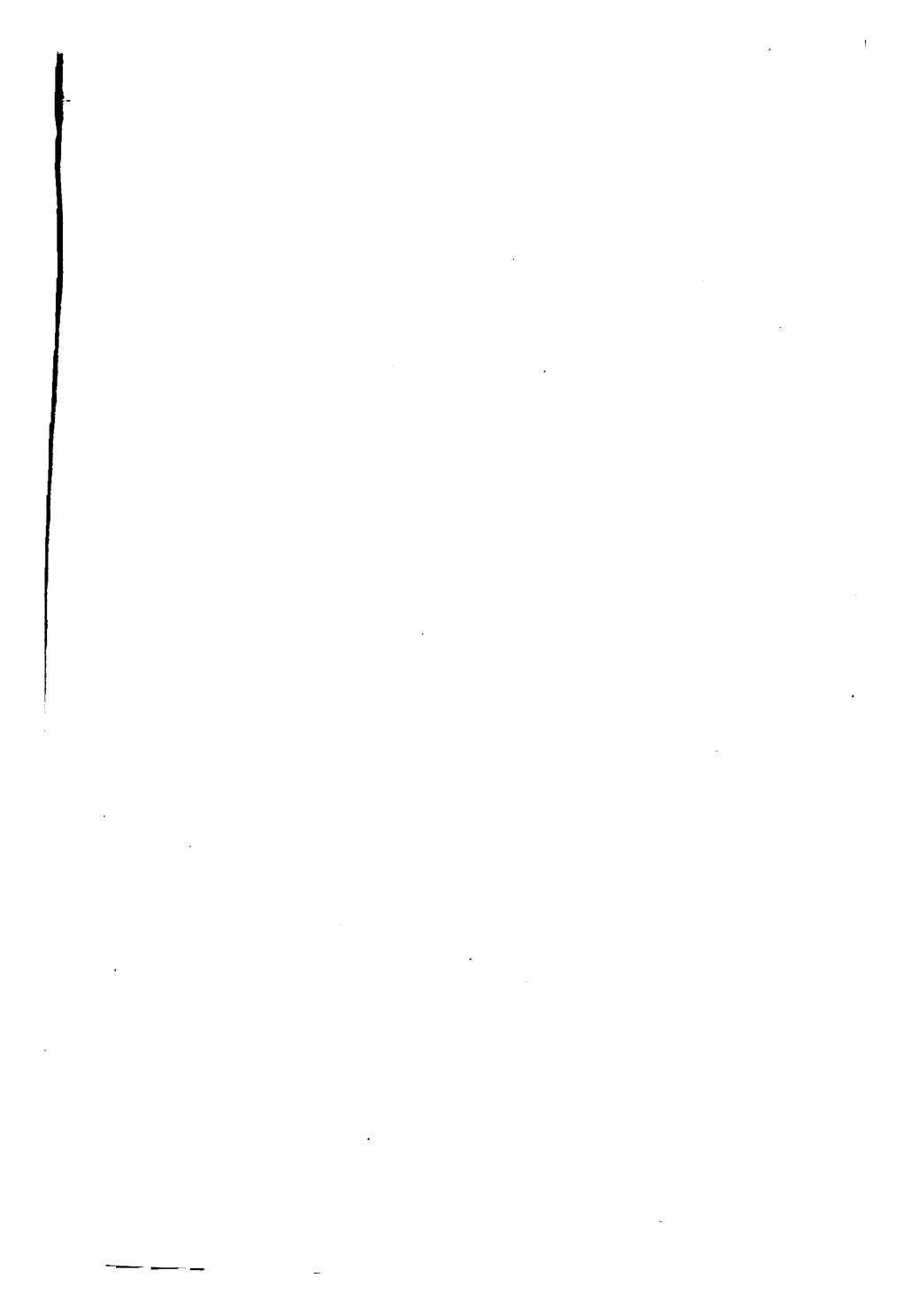
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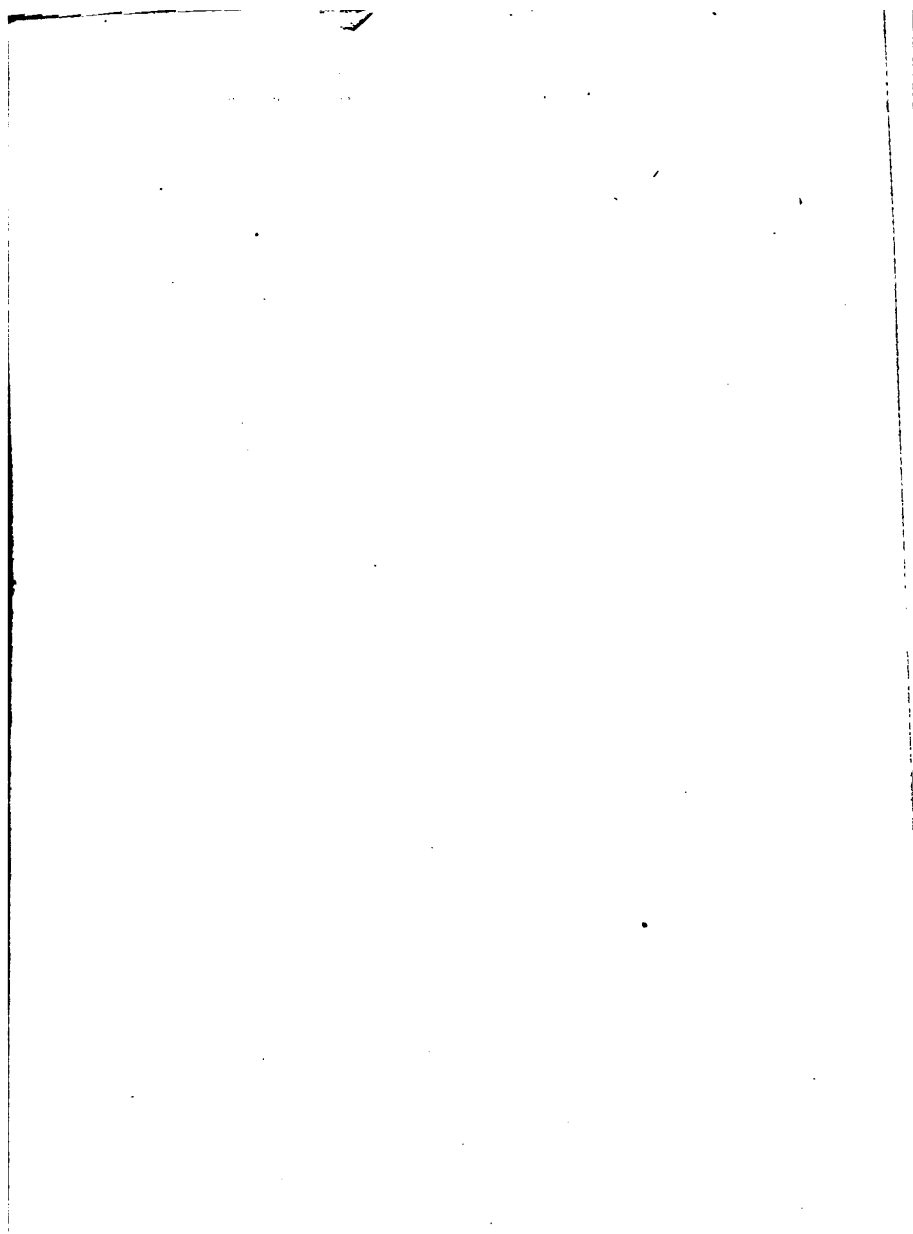
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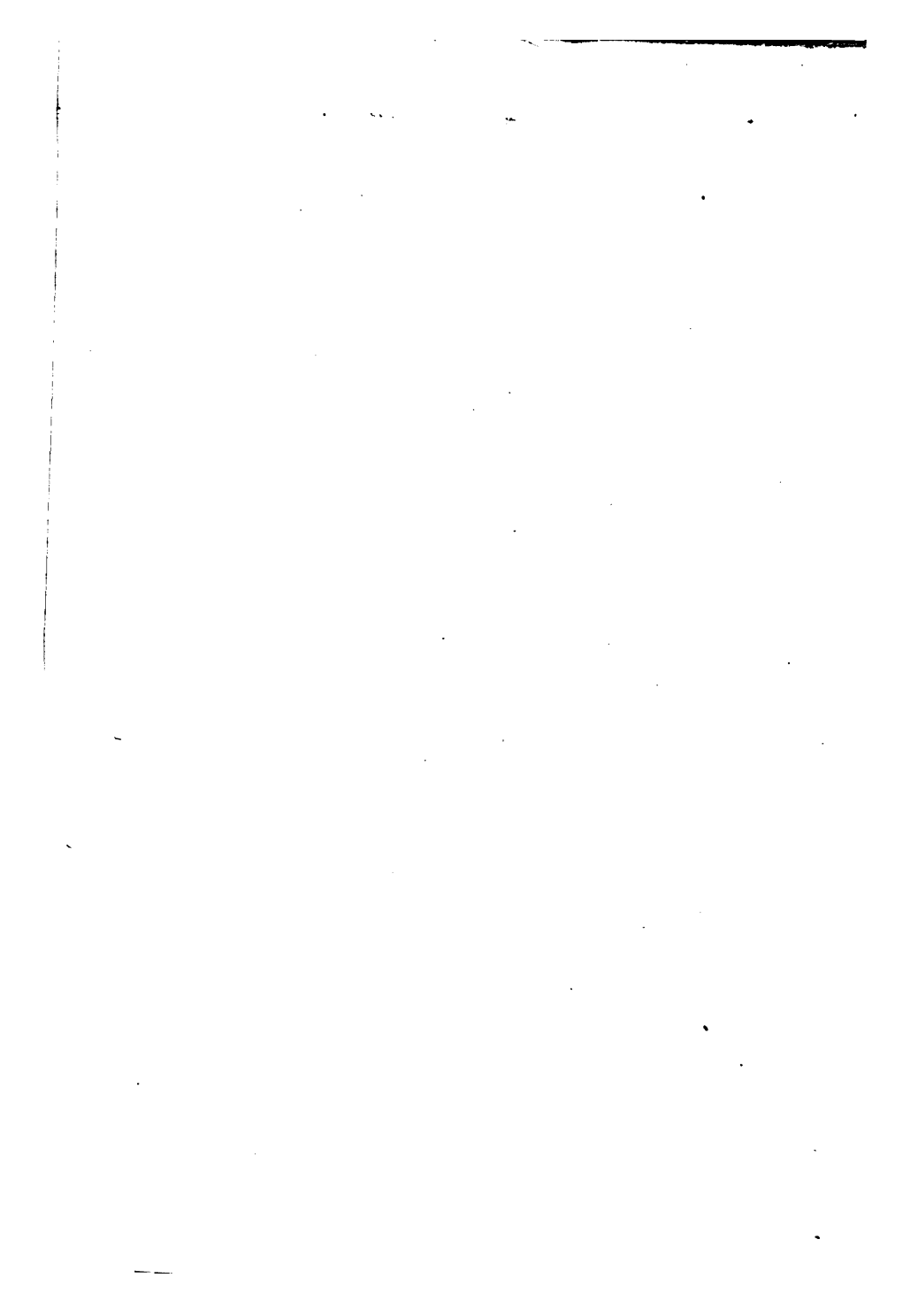
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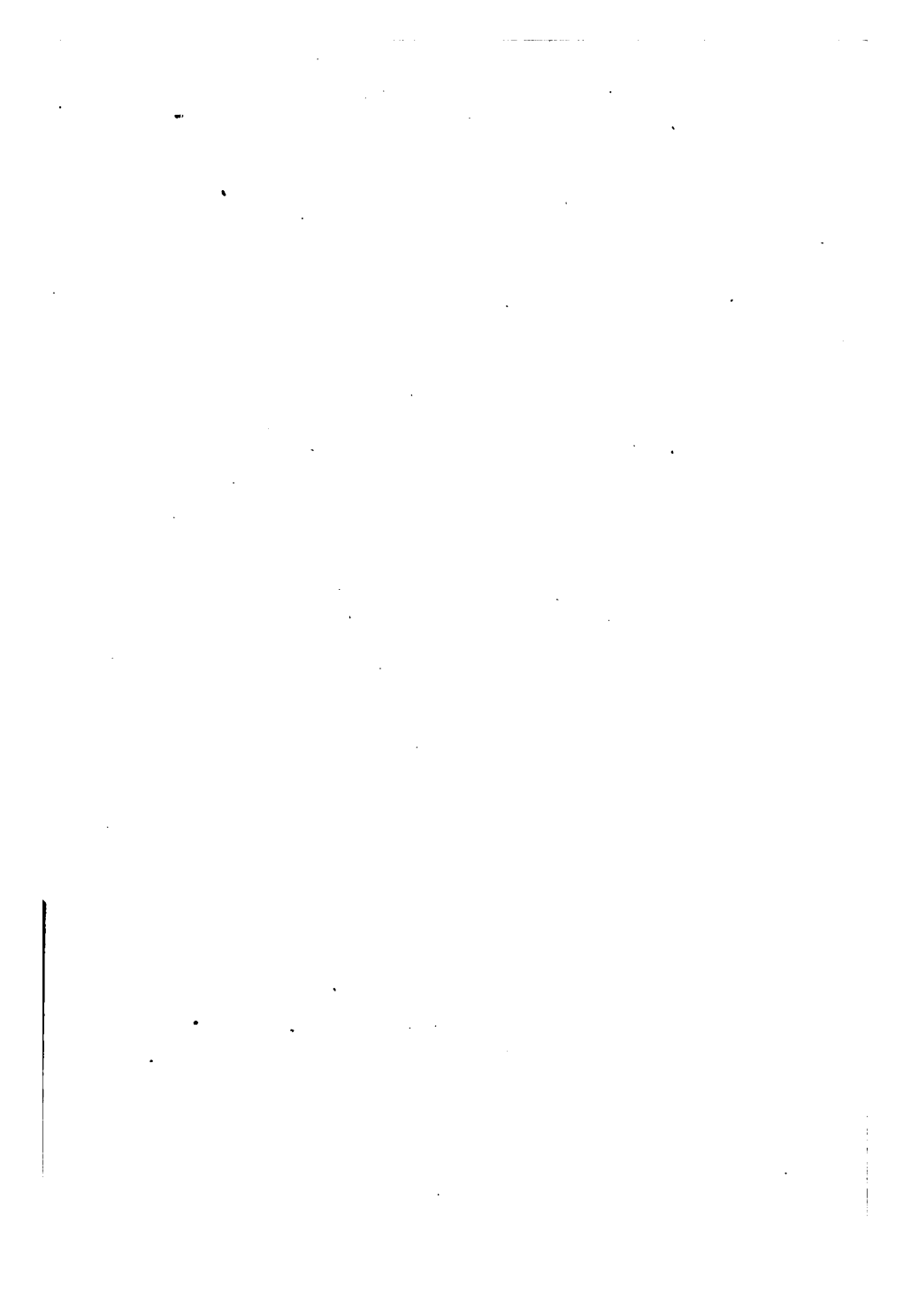
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AN INTRODUCTION TO THE STUDY  
OF  
CHEMISTRY

BY  
IRA REMSEN  
*President of The Johns Hopkins University*

EIGHTH EDITION, REVISED AND ENLARGED



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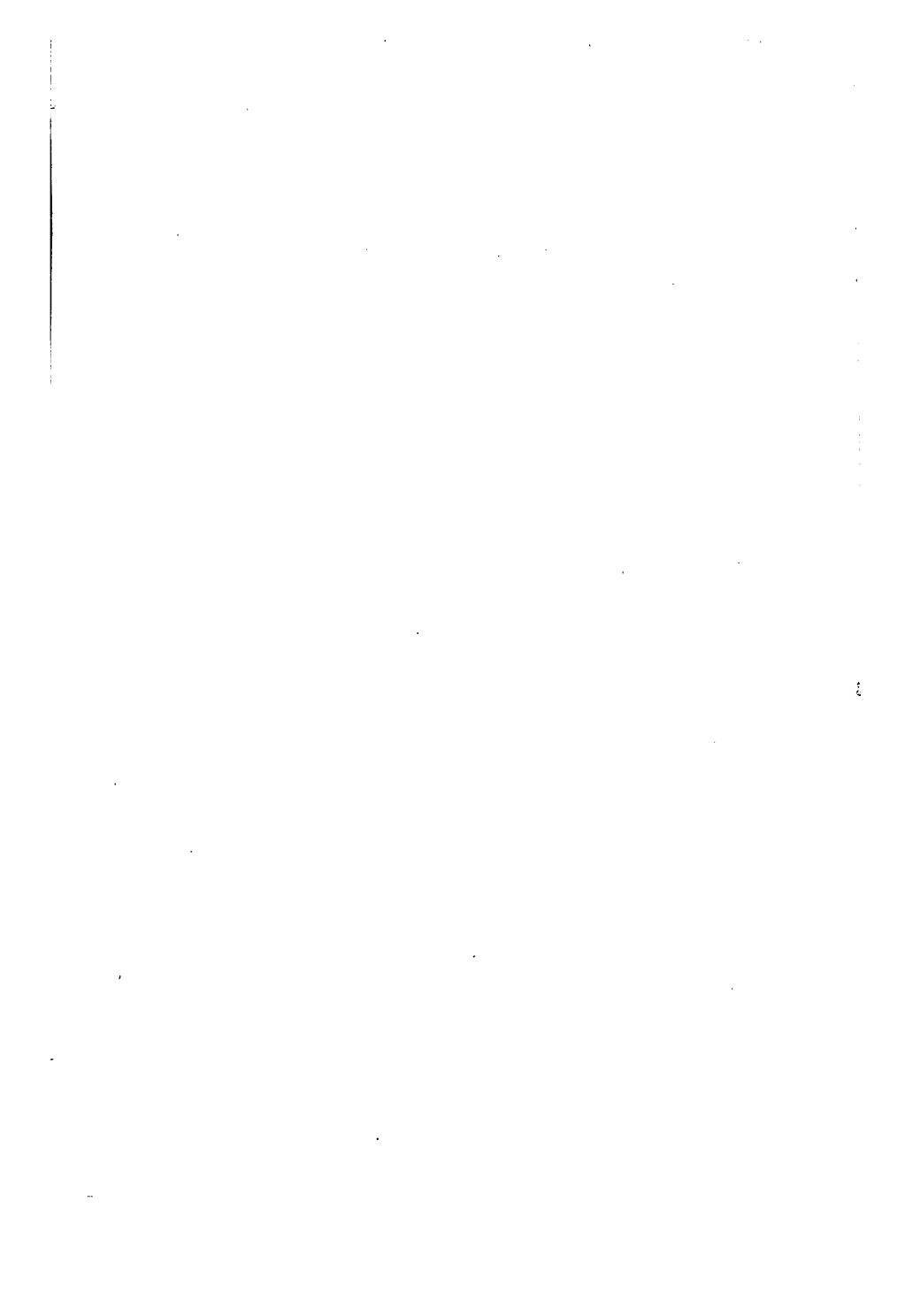


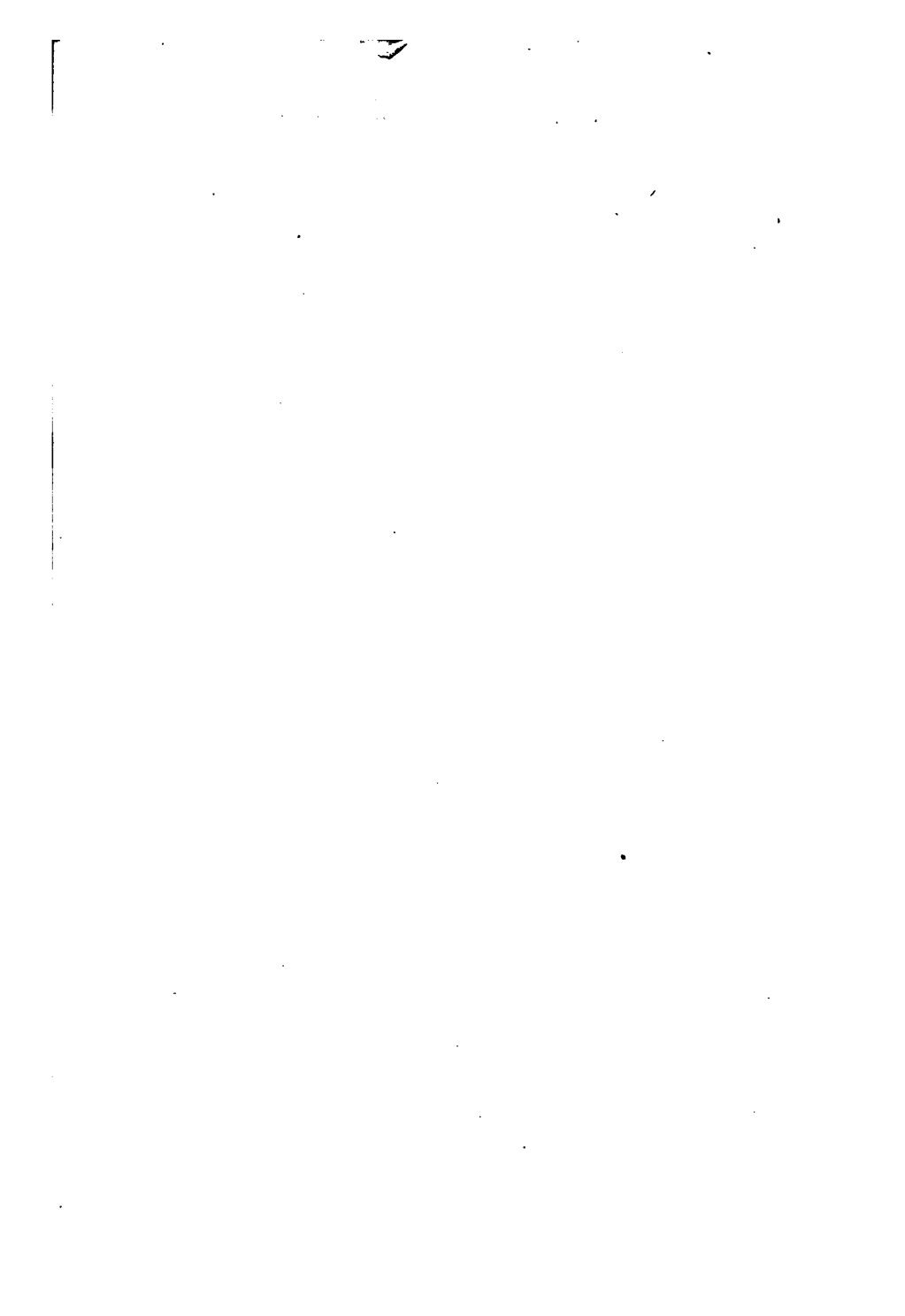
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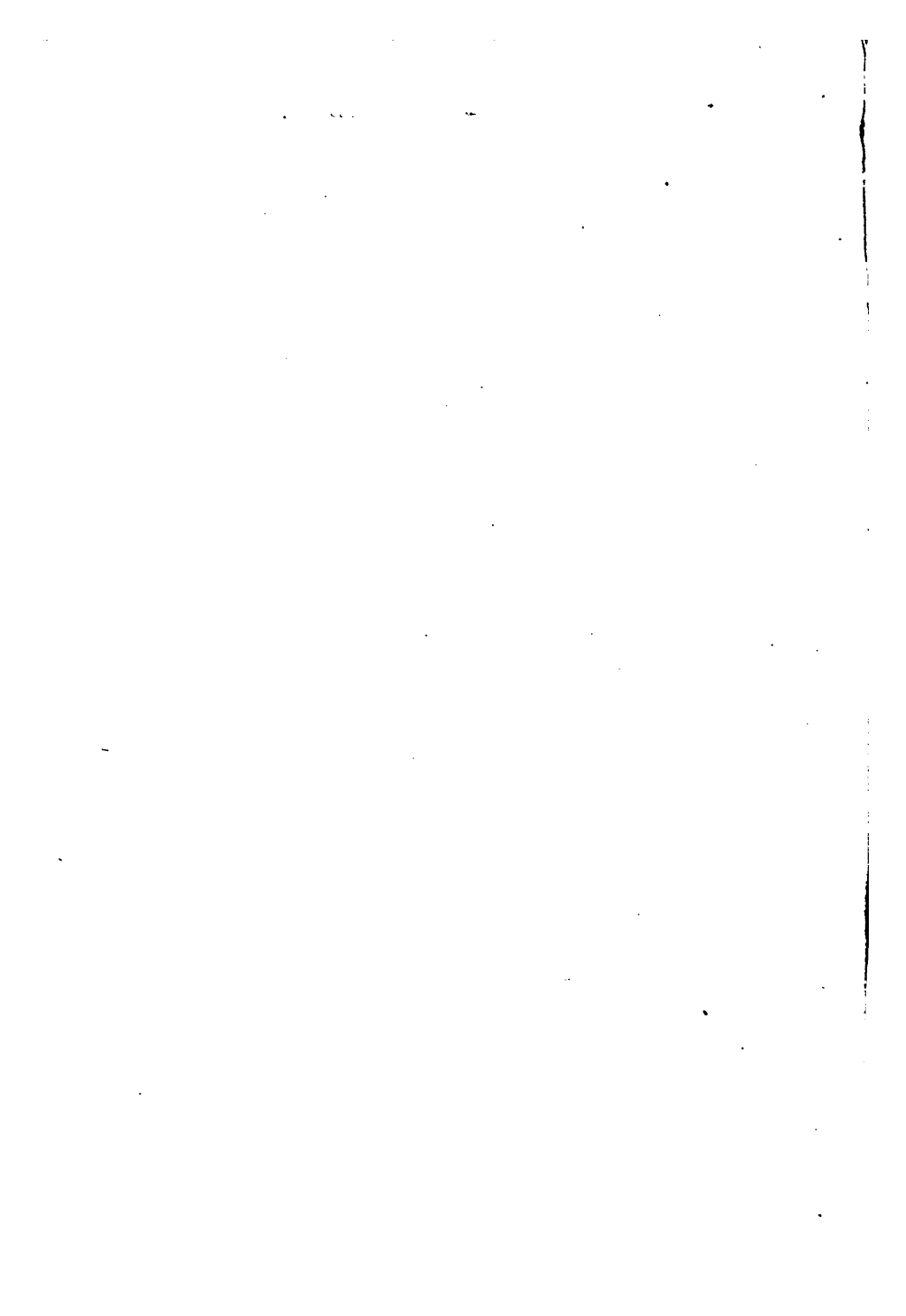
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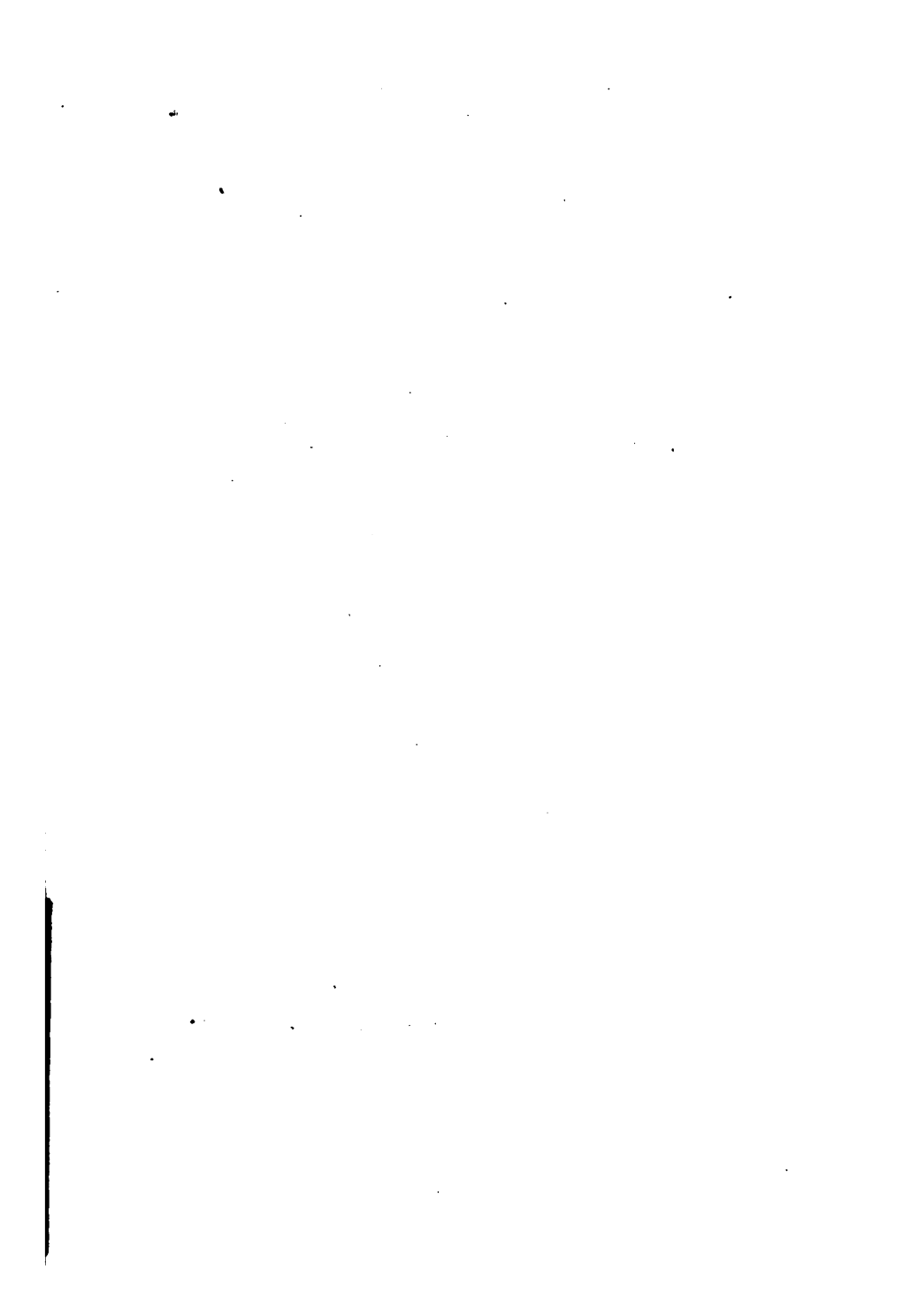
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## PREFACE TO THE THIRD EDITION.

THIS book has been thoroughly revised by me after seven years' experience with it in the laboratory and the classroom, and I believe that it will be found to be materially improved. In the work of revision I have been much aided by friends at home and abroad who have made valuable suggestions, all of which I have endeavored to consider without prejudice. Special attention has been given to the descriptions of the experiments, with the object of making them as clear and as suggestive as possible. A few which have been found to work unsatisfactorily have been omitted, and a few new ones have been added, among the latter being some of a quantitative character which have proved instructive where they have been tried, and it is hoped that, wherever the time will permit, they may be included in the regular course.

The principal changes made in the book besides those mentioned are:

1. A somewhat earlier introduction of the chapter on the atomic theory.
2. The presentation of the periodic law before the systematic study of the elements is taken up, and the classification of the elements in accordance with this law.

3. The addition of two chapters on some of the more common compounds of carbon.

4. The addition of a chapter on qualitative analysis.

5. A fuller treatment of the metallic elements.

6. The use of different type for the experiments and for the text; and clearer paragraphing.

I take pleasure in thanking my assistant, Dr. W. W. RANDALL, who has contributed to the value of the book by helping me in reading the proofs and by preparing the index.

I. R.

BALTIMORE, June, 1893.





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# AN INTRODUCTION TO THE STUDY OF CHEMISTRY.

## CHAPTER I.

### CHEMICAL ACTION.—ELEMENTS—COMPOUNDS.—HOW TO STUDY CHEMISTRY.

**Introductory.**—Those things which are most familiar to us are apt to be regarded with least wonder and to occasion the least thought. Take, for example, the changes included under the head of fire. Unless we have studied these changes with care, what can we make of them? We see substances destroyed by fire. They disappear for the most part. We feel the heat produced by the burning. We know that this heat disappears, and we have little left in the place of the substance burned. Take, as another example, the rusting of iron. We all know that iron when exposed to moist air undergoes a serious change, becoming covered with a reddish-brown substance called rust. If the piece of iron is comparatively thin, and it is allowed to lie in the air long enough, it will be completely changed to the reddish-

brown substance, and no iron as such will be left. If a spark is brought in contact with gunpowder there is a flash and the powder disappears, dense smoke appearing in its place. What are the causes of these remarkable changes? Can we learn anything about them by study?

**Chemical Changes.**—In those changes which have been referred to, the substances changed disappear as such. After the fire, the wood or the coal, or whatever may have been burned, is no longer to be found. The gunpowder after the flash is no longer gunpowder. The rusted iron is no longer iron, and, no matter how long the rust may be allowed to lie unmolested, it will not return to the form of iron. Iron may, further, be changed by contact with other substances than air so as to lose its properties. Strong vinegar, which contains the substance known to chemists as acetic acid, acts upon iron, causing it to lose its characteristic properties. The substances known as hydrochloric acid, nitric acid, and sulphuric acid also act upon iron and give rise to the formation of new substances which have not the properties of iron. Changes of this kind in which the substances disappear and something else is formed in their place are known as *chemical changes*, and chemistry is the science which has to deal with changes in the composition of substances.

**Physical Changes.**—There are, however, many changes taking place which *do not affect the composition* of substances. Iron, for example, may be changed in many ways and still remain iron. It may become hotter or colder. Its position may be changed. The difference between a piece of iron moving and a piece at rest is a very wonderful one,



though we are not, as a rule, much impressed by the difference. The iron may be struck in such a way as to cause it to give forth a sound. While giving forth the sound its condition is certainly different from that in which it does not give forth sound. The iron may be made so hot that it gives light. A piece of iron may be changed further by connecting it with a galvanic battery. We can easily recognize the difference between a piece of iron through which a current of electricity is passing and one through which no current is passing. Finally, when a piece of iron is brought in contact with a piece of loadstone, it acquires new properties. It now has the power to attract and hold to itself other pieces of iron. In all these cases, then, the iron is changed, but it remains iron. After the moving iron comes to rest it is exactly the same thing that it was before. After the iron which is giving forth sound has ceased to give forth sound, it returns to its original condition. Let the heated iron alone and it cools down, ceasing soon to give off light, and giving no evidence of being warm. Remove the iron from contact with the galvanic battery and it loses those properties which are due to the current of electricity. In time, the iron which is magnetized by contact with the loadstone loses its magnetic properties. Such changes are called *physical changes*.

**Physics and Chemistry.**—What is true of iron is true in general of all other substances. We see therefore from what has been said that there are two classes of changes presented to us for study:

1st. Those which do not affect the composition of substances.

2d. Those which affect the composition of substances and give rise to the formation of new substances with new properties.

Changes of the first kind are called *physical changes*. Those of the second kind are called *chemical changes*.

That branch of knowledge which has to deal with physical changes is known as PHYSICS; and that which has to deal with chemical changes is known as CHEMISTRY.

Everything that has to do with motion, with heat, light, sound, electricity, and magnetism, is studied under the head of Physics. Everything that has to do with the composition of substances and changes in the composition is studied under the head of Chemistry.

#### PHYSICAL CHANGE; CHEMICAL CHANGE.

*Experiment 1.*—Hold a piece of platinum wire in the flame of the laboratory burner for a moment. Remove it and hold it for a few moments in the air. What kind of change did it undergo in the flame? Was it a physical or chemical change? Hold a piece of magnesium ribbon in the flame by means of a pair of pincers. What kind of change takes place? Is it a physical or chemical change? Give reasons for your conclusions.—Mention some phenomena familiar to you that further illustrate these two kinds of change.

**Relations between the Different Kinds of Change.**—Although at first sight the different kinds of change referred to appear to be quite distinct from one another, they are, in reality, closely related. If a body in rapid motion is stopped suddenly, it becomes hot. Many examples of a similar transformation of motion into heat are familiar: a wire becomes hot when hammered on an anvil; a coin

rubbed on cloth becomes hot. In both cases the cause of the heat is the interference with the motion. The hammer is stopped and becomes hot; the coin is not stopped, but the motion is interfered with, and we have to push harder in order to move it over the cloth than we should to move it in the air. A wire through which a current of electricity is passing is heated, and if the wire is small and the current strong it will become so hot that it will give off light. Here the electricity causes heat and light. Again, we know that by means of heat we can produce motion. The steam-engine is the most familiar example of the transformation of heat into visible motion. We build a fire; this heats the water in the boiler; the water is converted into steam, which expands and moves the piston; and the motion of the piston is the seat of all the complex motions that take place in the different parts of the engine. The train or the ship moves. What moves it? Plainly, the heat is the cause of the motion. But we can go a step farther back and ask what causes the heat. The answer is obvious. It is the burning of the fuel. But, in burning, the composition of the fuel is completely changed. A change is produced which in itself is not heat. When a piece of coal burns, then, it is undergoing a change in composition, and, as a result of this change, heat is produced. The heat is, therefore, produced by a chemical change in the coal, and we may say that the motion of the steam-engine is the result of the chemical change taking place in the coal or wood which, in burning, produces the heat.

**Chemical Changes caused by Heat.**—Just as in all ordinary fires we have heat produced as a result of chemical changes

in the fuel, so we may have chemical changes produced by heat.

#### HEAT AND CHEMICAL CHANGE.

*Experiment 2.*—In a clean, dry test-tube put enough white sugar to make a layer  $\frac{1}{4}$  to  $\frac{1}{2}$  an inch thick. Heat gently in the flame of a spirit-lamp or a laboratory burner, as shown in Fig. 1.—

Describe what takes place. What is the appearance of the substance left in the tube? Is there any sugar left? After cooling, taste the mass. Has the sugar been changed physically or chemically? What has caused the change?



FIG. 1.

*Experiment 3.*—Put into a dry test-tube about 3 inches long and  $\frac{3}{8}$  inch in diameter enough red oxide of mercury (mercuric oxide) to form a layer about 12 millimeters ( $\frac{1}{2}$  inch) thick. Heat the tube as in the last experiment. During the heating thrust into the tube a splinter of wood which has a spark on the end. Take it out and put it back again a number of times.

What changes do you observe in the substance in the tube? What is deposited in the upper part of the tube? What takes place when the splinter with the spark is thrust into the tube?

#### Electric Currents connected with Chemical Changes.—

In a galvanic battery there are always substances that are undergoing changes in composition, and the electric current is the result of these changes. A simple form of a battery is represented in Fig. 2.

The plates marked *C* are of copper, those marked *Z* of zinc. The plates are connected by wires, as shown. A mixture of sulphuric acid and water is poured into each vessel. This mixture acts upon the zinc, causing a chemical change. The wire connecting the last plate of copper with

the first plate of zinc is found to have an electric current passing through it. This wire not only conducts the electric current, but also becomes heated.

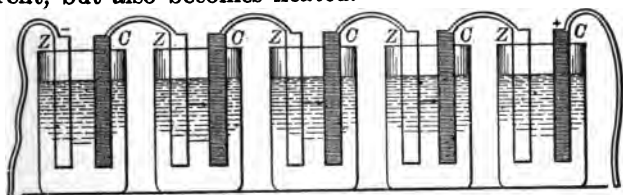


FIG. 2.

**Chemical Changes connected with the Passage of the Electric Current.**—This may be well illustrated by the action of an electric current on water.

#### THE ELECTRIC CURRENT AND CHEMICAL CHANGE.

*Experiment 4.*—(T) To the ends of the copper wires connected with two cells of a Bunsen's or Grove's battery fasten small platinum plates say 25 mm. (1 inch) long by 12 mm. ( $\frac{1}{2}$  inch) wide. Insert these platinum electrodes into water contained in a small shallow glass vessel about 15 cm. (6 inches) wide and 7 to 8 cm. (3 inches) deep, taking care to keep them separated from each other. No action will take place, for the reason that water will not conduct the current, and hence when the platinum electrodes are kept apart there really is no current. By adding to the water about one tenth its own volume of strong sulphuric acid, it acquires the power to convey the current. It will then be observed that bubbles rise from each of the platinum plates. In order to collect them an apparatus like that shown in Fig. 3 may be used.

*h* and *o* represent glass tubes which may conveniently be about 30 cm. (1 foot) long and 25 mm. (1 inch) internal diameter. They are first filled with the water containing one tenth its volume of sulphuric acid, and then placed with the mouth under water in the vessel *A*. The platinum electrodes are now brought beneath the inverted tubes. The bubbles which rise from them will pass upward in the tubes, and the water will be pressed down. Grad-

ually the water will be completely forced out of one of the tubes, while the other is still half full of water. The substances thus collected in each of the tubes are invisible gases. After the first tube is full of gas, place the thumb over its mouth and remove the tube. Turn it mouth upward and at once apply a lighted match to it. What takes place? Was the gas in the tube ordinary air? In the mean time the second tube will have become filled with gas. Remove this tube in the same way and insert a thin piece of wood with a spark on it. What do you observe?

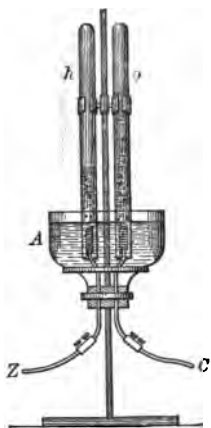


FIG. 3.

**Two Gases Formed.**—Without going into further details, it is clear from this experiment that when an electric current acts on water containing some sulphuric acid two invisible gases are produced. We shall have occasion hereafter to study this experiment much more carefully, and we shall find that from it we can learn a great deal more than we have just learned.

**Electrolysis.**—Such a process as that shown in the last experiment is called *electrolysis*. The ends of the wires connected with the battery are called *electrodes*. That electrode which is connected with the negative or zinc pole of the battery is called the *negative electrode* or *cathode*; while that electrode which is connected with the positive pole of the battery is called the *positive pole* or *anode*. By electrolysis is meant the chemical decomposition of a substance by the aid of an electric current.

**Collection of Gases.**—As it is frequently necessary in studying chemical changes to deal with gases, the student

should familiarize himself with the method adopted for collecting gases.

#### MANIPULATION OF GASES.

*Experiment 5.*—Fill a test-tube or glass cylinder with water; close its mouth with the thumb or a ground-glass plate; invert the tube, and put the mouth under water. The water stays in the tube after the thumb or glass plate is removed. (Why?) Now take a piece of glass or rubber tubing; put one end under the mouth of the inverted tube, and blow gently through the other end. Bubbles will rise in the tube and the water will be displaced. In this case the gases from the lungs are collected. When they come below the mouth of the tube, being lighter than water, they rise, and as the space occupied by them cannot be occupied by the water too, the latter is displaced. (See Fig. 4.)

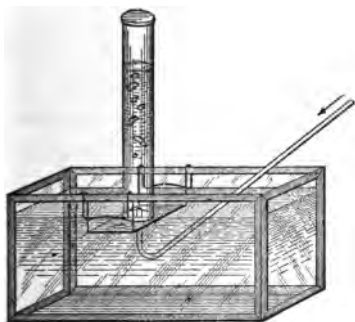


FIG. 4.

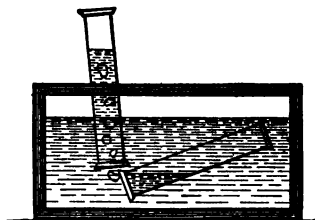


FIG. 5.

*Experiment 6.*—To transfer a gas from one vessel to another by displacement of water, place both vessels inverted in the same bath, and then gradually bring the one containing the gas, mouth upward, below the one containing the water. (See Fig. 5.)

**Relation between Chemistry and Physics.**—The experiments performed will suffice to show that the different kinds of changes, both the physical and the chemical, are

more closely related to one another than they appear to be at first sight. In consequence of this relation we cannot deal with chemical changes without constantly having to deal with physical changes. For a thorough understanding of chemical changes it is necessary to have some knowledge of the changes produced by heat and electricity. It will be found that whenever chemical changes take place, heat changes and sometimes electric changes also take place. And it will be found, too, that, in order to bring about chemical changes, use is frequently made of heat and electricity. If, therefore, the student has not studied physics, he should familiarize himself with a few of the elementary facts of the science before undertaking the study of chemistry. He should know what physical changes can be produced by heat; what boiling is; what evaporation is; what 'condensing a vapor' means; what the expression "to pass an electric current" means; how the more common forms of galvanic batteries are made, etc., etc. All these matters are of importance in studying chemical changes.

**Object of the Chemist's Study.**—Everything that has to do with the composition of substances is the object of the chemist's study. Most substances can by proper methods be separated into simpler ones, and these again into still simpler ones which cannot be further decomposed by any means known to us. Substances that cannot be decomposed into simpler ones by us are called *elements*.\* Now, although there are thousands of different substances, these are really made up of a comparatively small number of elements. The number of elements thus far discovered is

\* Recent investigations show that certain elements are slowly decomposing, yielding new elements as products of decomposition. See Uranium, p. 486.



between seventy and eighty, but most of these are rare. We shall find that most things we have to deal with are made up of about a dozen elements, and that most of the chemical changes that are taking place around us and that we need to study in order to get an insight into the nature of chemical action, take place between this small number of elements.

**Mechanical Mixtures.**—Most of the substances found in nature are made up of several others. Wood, for example, is very complex, containing a large number of distinct substances intimately mixed together. Some of these can be isolated, but it is impossible to isolate them all with the means at present at our command. Most rocks are also quite complex, and it is difficult to isolate the constituents. If we examine a piece of coarse-grained granite we see plainly enough that it contains different things mixed together, and if it is broken up we can pick out pieces of different substances from the mass. If we now examine a piece of each of the different substances, it appears to be homogeneous, *i.e.*, we cannot recognize the presence of more than one kind of thing in any one piece. If the piece is powdered, some of the powder can be examined with a microscope without the presence of more than one substance being recognized. We are able to isolate three substances from granite by simply breaking it up. We might therefore conclude that granite consists of three substances. This is true, but it is not the whole truth. For it is possible to get simpler substances from each of the three. This, however, is a much more difficult process than the separation first accomplished. Substances must be brought in contact with each of the three constituents

which change their composition, *i.e.*, act chemically upon them, and high heat must be used to aid the action. It is thus possible to separate the three components of granite into their elements.

Substances may then be united in different ways. They may be so united that it is a simple thing to separate them by mechanical processes. Or they may be so united that it is impossible to separate them by mechanical processes. By a mechanical process is meant any process that does not involve the use of heat, electricity, or chemical action. Thus, the mechanical process made use of in the case of granite consisted in picking out the pieces.

#### MECHANICAL MIXTURE.

*Experiment 7.*—Mix a gram or two of powdered roll-sulphur and an equal weight of very fine iron filings in a small mortar. Examine a little of the mixture with a microscope. Do you see both the sulphur and the iron?

Put aside some of this mixture for Ex. 10.

*Experiment 8.*—Pass a small magnet through the mixture above prepared. Unless the substances used are thoroughly dry, particles of sulphur will adhere to the magnet, but even then it will be seen that most of that which is taken out of the mixture is iron. This separation is a mechanical separation. It is a somewhat more refined method of picking out than that referred to in the case of the granite.

*Experiment 9.*—Pour a few cubic centimetres of carbon bisulphide on a little powdered roll-sulphur in a dry test-tube. Filter and let the solution evaporate on a watch-glass. What takes place?

In a second tube treat iron filings in the same way. Filter and evaporate. What takes place?

In a third tube treat a small quantity of a mixture of sulphur and iron filings with carbon bisulphide. After shaking for some

time let the tube stand quietly so that any solid suspended in the liquid may settle to the bottom. Then pass the liquid through a dry filter into a watch-glass. Let this watch-glass stand until the liquid has evaporated. Examine what remains undissolved in the test-tube. After the liquid has evaporated examine what is left on the watch-glass. What is in the test-tube? What on the watch-glass? Explain what has taken place.

A MECHANICAL MIXTURE CONVERTED INTO A CHEMICAL  
COMPOUND BY HEAT.

*Experiment 10.*—Put some of the mixture of powdered roll sulphur and fine iron filings prepared for Ex. 7 in a small dry test-tube. Heat sharply until the mass begins to glow, then take the tube out of the flame. After the mass has become cool, break the tube, and put the contents in a mortar. Break up the solid and examine it. Treat it with hydrochloric acid. Is it the same as the mixture before heating?

**The Product is a Chemical Compound.**—The new substance formed by the action of heat on the mixture of sulphur and iron is no longer a mechanical mixture. It cannot be decomposed by a mechanical process. The constituents are much more firmly united than they were in the mixture. They have lost their identity. They are both present, to be sure, but by means of an ordinary examination we cannot recognize them, as their characteristic properties have been lost. When the mixture began to glow, the act of combination began, and the glowing was a result of the act of combination. The sulphur and iron *combined with each other chemically*, and formed a *chemical compound*. They did not act upon each other when simply brought in contact. It was necessary to heat the mixture in order to cause chemical combination to take place. The

heat in this case helped the chemical action. But after the action began it continued without further aid and produced heat, as was shown by the glowing of the mass.

**One of the Chief Characteristics of Chemical Action.**—The essential feature of the action in the case of iron and sulphur, just studied, is this:

*The substances which act upon each other lose their individual properties and something is formed with entirely new properties.*

This is true of every case of chemical action, and it is one of the chief characteristics of that kind of action. If we should examine a number of cases of chemical action, we might be inclined to think that they had no common features; but this loss of properties and the formation of new substances always take place. A few examples will help to emphasize this truth.

#### CONTACT AND CHEMICAL CHANGE.

*Experiment 11.*—Examine a piece of calc-spar or of marble. Describe it. Heat a piece in a small glass tube, as in Experiment 5. Does it melt? Put a piece the size of a pea in a test-tube with distilled water. Thoroughly shake, and then, as heating usually aids solution, boil. Now pour off a few drops of the liquid on a piece of platinum \* foil or an evaporating dish, and by gently heating cause the water to evaporate. If there is anything solid in solution there will be a residue on the platinum foil or evaporating-dish. If not, there will be no residue. Is the substance soluble in water? Now treat a small piece (about the size of an ordinary marble) of the substance with dilute hydrochloric acid and notice what takes place. After the action has

\* Platinum, an expensive metal, finds extensive use in chemical laboratories, for the reason that it resists the action of heat and of most chemical substances.

continued for about a minute, insert a lighted match in the upper part of the tube. What takes place? Does the calc-spar dissolve? To determine whether anything else has taken place, we shall have to get rid of the excess of hydrochloric acid. This we can easily do by boiling it, when it passes off in the form of vapor and then whatever is in solution will remain behind. For this purpose put the solution in a small, clean porcelain evaporating-dish, and put this on a vessel containing boiling water, or a water-bath. The operation should be carried on in a place in which the draught is good, so that the vapors will not collect in the working-room. They are not poisonous, but they are annoying. The arrangement for evaporating is represented in Fig. 6.

After the liquid has evaporated and the substance in the evaporating-dish is dry, examine it and carefully compare its properties with those of the substance which was put into the test-tube. How does it differ in appearance from this? Is it harder or softer? Is it soluble in water? Does it melt when heated in a dry tube? Does it give off bubbles of gas when treated with hydrochloric acid? Let some of it stand in contact with the air. What change takes place?



FIG. 6.

**What this Experiment Shows.**—The experiment shows that when hydrochloric acid acts upon calc-spar or marble, the latter at least loses its own properties. It might be shown that some of the hydrochloric acid also loses its properties. In place of the two we get a new substance with entirely different properties. The two substances have acted chemically upon each other and produced a chemical compound different from either. In this case it was only necessary to bring the substances in contact in order to

cause them to act chemically upon each other. It was not necessary to heat them, as it was in the case of the iron and sulphur.

#### OTHER EXAMPLES OF CHEMICAL CHANGE.

*Experiment 12.*—Bring together in a test-tube a few small pieces of copper and some moderately dilute nitric acid. What takes place? Do not inhale the gas. Describe the changes in the color of the liquid. Does the copper dissolve? Examine this solution, as in Experiment 11, and see what has been formed. What are the properties of the substance found after evaporation of the liquid? Is it colored? Is it soluble in water? Does it change when heated in a tube? Is it hard or soft? Does it in any way suggest the copper with which you started?

*Experiment 13.*—Try the action of dilute sulphuric acid on a little zinc in a test-tube. Apply a lighted match to the mouth of the tube. Does the result suggest anything noticed in an experiment already performed? What is the meaning of the bubbling of the liquid? After the zinc has disappeared evaporate the solution as in Experiments 11 and 12. Carefully compare the properties of the substance left behind with those of zinc.

*Experiment 14.*—Hold the end of a piece of magnesium ribbon about 20 centimetres (8 inches) long in a flame until it takes fire; then hold the burning substance quietly over a piece of dark paper, so that the light, white product may be collected. Compare the properties of this white product with those of the magnesium. Here again a chemical act has taken place. The magnesium has combined with something from the air, and heat was produced by the combination. The product is the white substance (compare Exp. 1).

*Experiment 15.*—In a dry, wide test-tube put a bit of granulated tin. Pour upon it 2 or 3 ccm. concentrated nitric acid. If no change takes place, heat gently and presently there will be a copious evolution of a reddish-brown gas with a disagreeable smell. (Under what conditions has a gas like this already been obtained?) What appears in place of the tin? Compare

the properties of the new substance with those of tin. Why are you justified in concluding that they are not the same thing?

**General Conclusion.**—Experiments like those just performed might be multiplied to any extent desired. But a sufficient number have already been studied to show upon what kinds of observations is based the statement that

*Whenever two or more substances act upon one another chemically they lose their characteristic properties, and new substances with new properties are formed.*

**The Cause of Chemical Action.**—It is evident from what has already been learned that there is some power that can hold substances together in a very intimate way, so intimate that they cannot be recognized by ordinary means. We do not know what causes the sulphur and iron to combine, but we know that they do combine. Similarly, we do not know what causes a stone thrown upward in the air to fall back again, but we know that it falls back. It is true, we may say and do say that the cause of the falling of the stone is the *attraction of gravitation*, but this does not give us any information, for if we ask what the attraction of gravitation is, we can only answer that it is that which causes all bodies to attract one another. We can also give the name *chemical affinity* or *chemism* to that which causes chemical combination, but this does not help us to *understand what this cause is*. All the chemical changes that are taking place around us may be referred to this cause, whatever it may be. If this cause should suddenly cease to operate, what would be the result? Nature would be infinitely less complex than it now is. All substances now known to be *chemical compounds* would be resolved into the elements of which they are composed, and, as far as we know, there would be

only about seventy or eighty different kinds of substances. All living things would cease to exist, and in their place we should have three invisible gases, and something very much like charcoal. Mountains would crumble to pieces. All water would disappear, giving two invisible gases. The processes of life in its many forms would be impossible, for, however subtle that which we call life may be, we cannot imagine it to exist without the existence of certain complex forms of matter; and, as regards the life-processes of larger animals and plants, most complex chemical changes are constantly taking place within them, and these changes are absolutely essential to the continuation of life.

**Summary.**—We have thus far learned the difference between physical and chemical change. We have learned the difference between elements and chemical compounds, and between chemical compounds and mechanical mixtures. We have learned that there is a close relation between the different kinds of physical change and chemical change; and that one kind of change is capable of causing other kinds. We have learned how to distinguish chemical action from other kinds of action, the loss of their own properties which the substances suffer being a prominent characteristic of chemical action.

**How to Study Chemistry.**—We might learn a great deal about the facts of chemistry and learn very little in regard to the *science* of chemistry. As long as we do not recognize any connection between the facts observed we cannot properly speak of a subject as a science. The subject must have been studied for a long time. The laws governing some of the phenomena of the subject must have been discovered before that subject can be regarded as a science.



Before we can have any conception of the science of chemistry we must become acquainted with some of the most important facts of the science, and we must also learn what connection exists between these facts. We must become familiar with substances as they are, but especially with the way they act upon one another. Unfortunately for our purpose, but very few simple substances or elements occur in the uncombined form in nature. While, therefore, the simplest way to begin the study of chemical substances and chemical changes is by an examination of the elements, the subject is complicated by the fact that these elements cannot readily be obtained without the aid of substances which have not been studied and of processes which it is difficult to understand without some knowledge of chemistry. There are, however, two elements that occur in nature in enormous quantities and that can be obtained in the uncombined condition very easily. As the kinds of action which these exhibit are of great importance and give an insight into the nature of chemical action in general, the study of chemical phenomena may be profitably begun by the study of these two elements. They are oxygen and hydrogen. In studying the main facts in regard to these elements much will be learned that will be of service in making other chemical phenomena comprehensible.

**The Elements and their Symbols.**—Before beginning this study a list of the elementary substances thus far discovered is here given. The names of those which are most widely distributed, and which form by far the largest part of the earth, are printed in small capitals. The names of those which are very rare are printed in italics. As has

been stated, not more than a dozen elements enter largely into the composition of the earth. It has been calculated that the solid crust of the earth is made up approximately as represented in the subjoined table:

Oxygen.....	47.29%	Calcium.....	3.77%
Silicon.....	27.21%	Magnesium.....	2.68%
Aluminium.....	7.81%	Sodium.....	2.36%
Iron.....	5.46%	Potassium.....	2.40%

While oxygen forms a large part of the solid crust of the earth, it forms a still larger part (eight ninths) of water by weight, and about one fifth of the air by volume. Carbon is the principal element entering into the structure of living things, while hydrogen, oxygen, and nitrogen are also essential constituents of animals and plants. Nitrogen forms about four fifths of the air by volume.

In representing the results of chemical action it is convenient to use abbreviations for the names of elements and compounds. Thus, instead of oxygen we may write simply O, for hydrogen H, for nitrogen N, etc. These symbols are used in representing what takes place when substances act upon one another, as will be shown more clearly hereafter. Frequently the first letter of the name of the element is used as the symbol. If the names of two or more elements begin with the same letter, this letter is used, but some other letter of the name is added. Thus, B is the symbol of boron, Ba of barium, Bi of bismuth, etc. In some cases the symbols are derived from the Latin names of the elements. Thus, the symbol for iron is Fe, from Latin *ferrum*; for copper, Cu, from *cuprum*; for mercury, Hg, from *hydrargyrum*, etc. The symbols of the more common elements will soon become familiar by use. It is not desirable to attempt to commit them to memory.

The names themselves are derived from a variety of circumstances. Chlorine is derived from *χλωρὸς*, which means yellowish green, as this is the color of chlorine. Bromine comes from *βρῶμος*, a stench, a prominent characteristic of bromine being its bad odor. Hydrogen comes from *ὕδωρ*, water, and *γένειν*, to produce, signifying that it is a constituent of water. Similarly nitrogen comes from *νίτρον*, nitre, and *γένειν*, to produce, nitrogen being one of the constituents of nitre. Potassium is an element found in potash, and sodium is found in soda.

## LIST OF THE ELEMENTS AND THEIR SYMBOLS.

<i>Actinium</i> .....Ac	<i>Helium</i> .....He	<i>Rhodium</i> .....Rh
ALUMINIUM.....Al	HYDROGEN.....H	<i>Rubidium</i> .....Rb
Antimony.....Sb	Indium.....In	<i>Ruthenium</i> .....Ru
<i>Argon</i> .....A	Iodine.....I	<i>Samarium</i> .....Sa
Arsenic.....As	Iridium.....Ir	<i>Scandium</i> .....Sc
Barium.....Ba	IRON.....Fe	<i>Selenium</i> .....Se
Bismuth.....Bi	<i>Krypton</i> .....Kr	SILICON.....Si
Boron.....B	<i>Lanthanum</i> .....La	Silver.....Ag
Bromine.....Br	Lead.....Pb	SODIUM.....Na
Cadmium.....Cd	Lithium.....Li	Strontium.....Sr
<i>Cæsium</i> .....Cs	MAGNESIUM.....Mg	Sulphur.....S
CALCIUM.....Ca	Manganese.....Mn	<i>Tantalum</i> .....Ta
CARBON.....C	Mercury.....Hg	<i>Tellurium</i> .....Te
<i>Cerium</i> .....Ce	Molybdenum.....Mo	<i>Thallium</i> .....Tl
CHLORINE.....Cl	<i>Neodymium</i> .....Nd	<i>Thorium</i> .....Th
Chromium.....Cr	<i>Neon</i> .....Ne	<i>Thulium</i> .....Tu
Cobalt.....Co	Nickel.....Ni	Tin.....Sn
<i>Columbium</i> .....Cb	NITROGEN.....N	Titanium.....Ti
Copper.....Cu	<i>Osmium</i> .....Os	Tungsten.....W
<i>Erbium</i> .....E	OXYGEN.....O	Uranium.....U
Fluorine.....F	Palladium.....Pd	Vanadium.....V
<i>Gadolinium</i> .....Gd	Phosphorus.....P	<i>Xenon</i> .....X
<i>Gallium</i> .....Ga	Platinum.....Pt	<i>Ytterbium</i> .....Yb
<i>Germanium</i> .....Ge	POTASSIUM.....K	<i>Yttrium</i> .....Y
Glucinum.....Gl	<i>Praseodymium</i> .....Pr	Zinc.....Zn
Gold.....Au	<i>Radium</i> .....Ra	Zirconium.....Zr

## LIST OF ELEMENTS TREATED OF IN THIS BOOK.

ALUMINIUM.	Gold.	Platinum.
Antimony.	<i>Helium.</i>	POTASSIUM.
<i>Argon.</i>	HYDROGEN.	<i>Radium</i>
Arsenic.	Iodine.	<i>Selenium.</i>
Barium.	IRON.	SILICON.
Bismuth.	<i>Krypton.</i>	Silver.
Boron.	Lead.	SODIUM.
Bromine.	MAGNESIUM.	Sulphur.
CALCIUM.	Manganese.	<i>Tellurium.</i>
CARBON.	Mercury.	Tin.
CHLORINE.	<i>Neon.</i>	Uranium.
Chromium.	Nickel.	<i>Xenon.</i>
Cobalt.	NITROGEN.	Zinc.
Copper.	OXYGEN.	
Fluorine.	Phosphorus.	

Of these argon, helium, krypton, neon, radium, and xenon are but briefly mentioned, as they occur in very small quantity and do not take part in ordinary chemical changes.

## CHAPTER II.

### A STUDY OF THE ELEMENT OXYGEN.

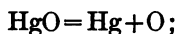
IN Experiment 4 it was shown that when an electric current is passed through water containing sulphuric acid two gases are liberated. One of these is distinguished by the readiness with which substances burn in it. This gas is oxygen. A gas with the same properties was also obtained by heating the red oxide of mercury. This is, in fact, the same substance.

**Occurrence of Oxygen.**—Oxygen is the most widely distributed element, and it occurs also in very large quantity. It has been stated that it forms nearly fifty per cent of the solid crust of the earth, eight ninths of water, and about one fifth of the air.

**Discovery of Oxygen.**—Oxygen was discovered in 1774 by Scheele in Sweden and by Priestley in England. Scheele obtained it by heating saltpetre (which see), and Priestley by heating the red oxide of mercury (mercuric oxide).

**Preparation of Oxygen.**—Oxygen is generally obtained by heating certain substances that contain it. The simplest example of this kind is that furnished by the oxide of mercury, which when heated yields mercury and oxygen. If the

oxide is weighed, and, after decomposition, the oxygen and the mercury are weighed, the weight of the mercury plus the weight of the oxygen will be found to be equal to the weight of the oxide. Therefore the oxide contains only mercury and oxygen. They are chemically combined. When the temperature is raised sufficiently the compound is resolved into its elements. The chemical compound which contains mercury and oxygen is represented by writing the symbols of the two elements side by side, thus,  $\text{HgO}$ , which signifies primarily that the two elements are in chemical combination. To represent what takes place when the oxide is heated this equation is used:



which is read, mercuric oxide gives mercury and oxygen.

**Preparation of Oxygen from Potassium Chlorate.**—Another substance that readily gives up oxygen when heated is potassium chlorate. This is a white, crystallized substance that is manufactured in large quantity and is sold at a low price. It contains the elements chlorine, oxygen, and potassium. When heated to a sufficiently high temperature it gives off all its oxygen, a compound of potassium and chlorine being left behind. The chemical changes brought about in potassium chlorate by heating it are interesting, and they will be studied somewhat in detail a little later. At present they are of interest mainly because they furnish the element oxygen.

#### OXYGEN FROM POTASSIUM CHLORATE.

*Experiment 16.*—(tt) Arrange an apparatus as shown in Fig. 7. *A* represents a retort of about 100 ccm. capacity. *B* is a piece of

rubber tubing which in turn is connected with a piece of glass tubing bent upward at the end. This end is placed under the surface of the water in *C*. In *A* put 2 to 3 grams (about a sixteenth of an ounce) potassium chlorate, and gently heat by means of the lamp. Notice carefully what takes place. At first the potassium chlorate will melt, forming a clear liquid. If the temperature is raised, the liquid will appear to boil, and it will soon be seen that a gas is being given off. Now bring the inverted cylinder *E* filled with water over the end *D* of the tube, and let the bubbles of gas rise in the cylinder. After a considerable

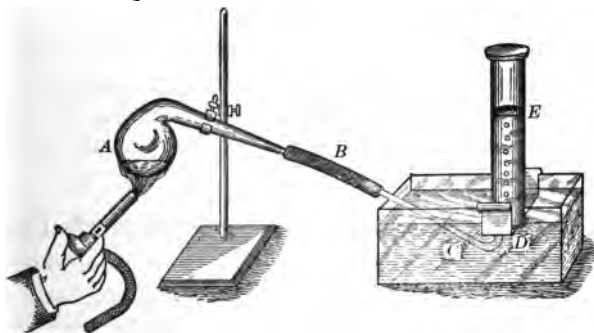


FIG. 7.

quantity of gas has been collected in this way the action stops, the mass in the flask becomes solid, and apparently the end of the process is reached. But if the heat is raised still higher, gas will again come off, and in this second stage a larger quantity will be collected than in the first. Finally, however, the end is reached, and the substance left in the flask remains unchanged, no matter how long heat may be applied. Examine the gas as in Experiments 3 and 4, pages 6 and 7. It will be shown later, page 99 that in the first stage of the decomposition of potassium chlorate the products are potassium perchlorate and oxygen, and that in the second stage the potassium perchlorate is decomposed into potassium chloride and oxygen, so that the final products of the action are potassium chloride and oxygen.

**Oxygen from Manganese Dioxide.**—Another good method for preparing oxygen consists in heating black oxide of manganese. This is a compound found in nature, called by mineralogists pyrolusite, and by chemists manganese dioxide. It consists of the elements manganese and oxygen. When this substance is heated it loses part (see page 100) of its oxygen, and there is left behind another compound of manganese and oxygen containing the elements in different proportions.

#### OXYGEN FROM MANGANESE DIOXIDE.

*Experiment 17.*—Make oxygen by heating to redness 3 to 4 grams (about an eighth of an ounce) of manganese dioxide in a hard-glass tube closed at one end and connected at the other end by means of a cork with a bent glass tube.

**Oxygen from Potassium Chlorate and Manganese Dioxide.**—The method most commonly employed in making oxygen in the laboratory consists in heating a mixture of equal parts by weight of potassium chlorate and manganese dioxide. This mixture gives off oxygen readily when heated. The oxygen comes from the potassium chlorate. The manganese dioxide takes part in the decomposition, but remains behind finally in its original form. It causes the potassium chlorate to give up its oxygen at a lower temperature than it does when heated alone. The chemical changes involved are quite complicated and cannot be studied profitably at this stage.

#### OXYGEN FROM POTASSIUM CHLORATE AND MANGANESE DIOXIDE.

*Experiment 18.*—Mix 25 to 30 grams (or about an ounce) of coarsely powdered potassium chlorate with an equal weight of coarsely powdered manganese dioxide in a mortar. The sub-



stances should not be in the form of fine powder. Test the mixture by heating a small quantity of it in a dry test-tube. If the decomposition takes place quietly, put the mixture in a dry retort, arranged as shown in Fig. 7, heat it, and collect the gas by displacement of water in appropriate vessels,—cylinders, bell-jars,

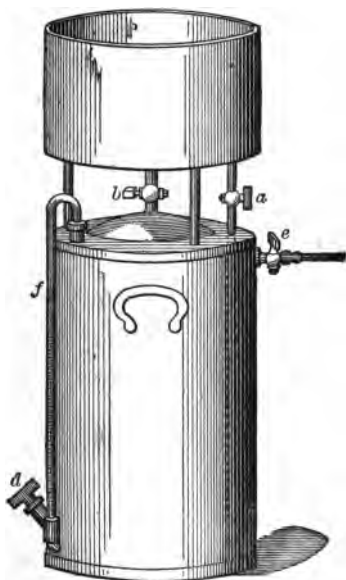


FIG. 8.

bottles with wide mouths, etc. It will also be well to collect some in a gasometer, such as is commonly found in chemical laboratories, the essential features of which are represented in Fig. 8. It is made either of metal or of glass. The opening at *d* can be closed by means of a screw-cap. In order to fill it with water open the stop-cocks and pour the water into the upper part of the vessel after having screwed the cap on to *d*. When it is full, water will flow out of the small tube *e*. Now close all the stop-cocks, and take the cap from *d*. The water will stay in the vessel for the

same reason that it will stay in the cylinder inverted with its mouth below water. To fill the gasometer with gas, put it over a tub or sink and introduce the tube from which gas is issuing into the opening at *d*. The gas will rise and displace the water, which will flow out at *d*. When full, screw the cap on. To get the gas out of the gasometer, attach a rubber tube to *e*, pour water into the upper part of the gasometer, open the stop-cock *a* and that at *e*, when the gas will flow out, and the current can be regulated by means of the stop-cock at *e*.

**Oxygen from "Oxone."**—"Oxone" consists essentially of sodium peroxide,  $\text{Na}_2\text{O}_2$  (which see). When it is treated with water oxygen is at once given off. This is the simplest way to make oxygen.

#### OXYGEN FROM "OXONE."

*Experiment 19.*—If oxone is available throw a piece the size of an ordinary marble into about 100 ccm. water contained in a glass cylinder. Test the gas given off. Does it act like oxygen?

**Physical Properties of Oxygen.**—In the first place, the gas is invisible. The slight cloud which appears in the vessels when the gas is first collected will disappear if the vessels are allowed to stand for a few minutes, and the vessels will look as if they were filled with air. The gas is tasteless and inodorous.

Oxygen is slightly heavier than the air. This can be determined by weighing a dry globe filled with air, then driving out the air by passing a current of oxygen through it for some time, and weighing it again. If these weighings are carefully made, it will be found that the relation between the weights of equal volumes of air and oxygen is 1:1.1056. Or, in other words, if a certain volume of air weighs 1 gram, the same volume of oxygen will weigh 1.1056 grams. When

gaseous oxygen is subjected to high pressure and a temperature below  $-119^{\circ}$ , it is converted into a blue liquid which boils at  $-182.8^{\circ}$ . (See LIQUID AIR.)

The properties of oxygen to which reference has thus far been made are its *physical properties*. These are its appearance, taste, smell, relative weight, and changes in its condition, which still leave it in the elementary form uncombined chemically. Our knowledge of oxygen must, of course, include a knowledge of its physical properties, but, from the chemical point of view, it is more important for us to know how oxygen acts chemically. What chemical changes is it capable of bringing about? What conditions are necessary in order that it may act chemically? What laws govern the action? What products are formed?

**Chemical Conduct of Oxygen.**—In order to learn how oxygen acts upon some simple substances under ordinary circumstances, we may perform a few experiments.

#### CHEMICAL CONDUCT OF OXYGEN.

*Experiment 20.*—Turn three of the bottles containing oxygen with the mouth upward, leaving them covered with glass plates. Into one introduce some sulphur in a deflagrating-spoon, which is a small cup of iron or brass attached to a stout wire that passes through a round metal plate, usually of tin. (See Fig. 9.) In another put a little charcoal (carbon), and in a third a piece of phosphorus\* about the size of a pea. Let them stand quietly and notice what changes, if any, take place. Sulphur, carbon, and phosphorus are elements, and oxygen is an element. It

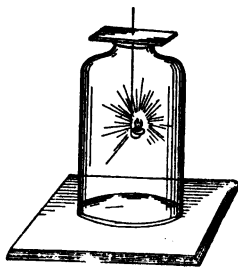


FIG. 9.

\* Phosphorus should be handled with great care because it takes

will be noticed that the sulphur and the carbon remain unchanged, while some change takes place in the phosphorus, as is shown by the appearance of white fumes in the vessel containing it. After some time the phosphorus will disappear entirely, the fumes will also disappear, and there will be nothing visible to show us what has become of the phosphorus. If the temperature of the room is rather high, it may happen that the phosphorus will take fire. If it should, it will burn with an intensely bright light. After the burning has stopped, the vessel will be filled with white fumes, but these will gradually disappear, and the vessel will apparently be empty.

**What these Experiments Show.**—These experiments show that oxygen does not act upon sulphur and carbon when brought in contact with them at the ordinary temperature, and that the action upon phosphorus is generally slight. We might perform experiments of this kind with a great many substances, and we should reach the conclusion that at ordinary temperatures oxygen does not act upon most substances.

**Action of Oxygen at Higher Temperatures.**—If, however, the substances are heated before they are introduced into the oxygen, the results will be entirely different. Instead of conducting itself as an inactive element, oxygen will act with great ease upon many substances. Things such as coal, wood, etc., which we know will burn in the fire easily and phosphorus burns are painful and hard to heal. Such burns should be treated with a paste of sodium carbonate and water. Phosphorus is always kept under water, usually in the form of sticks. If a small piece is wanted, take out a stick with a pair of forceps, and put it under water in an evaporating-dish. *While it is under the water*, cut off a piece of the size wanted. Take this out by means of a pair of forceps, lay it for a moment on a piece of filter-paper, which will absorb most of the water, then quickly put it in the spoon.

air, burn in oxygen much more readily, and several substances such as iron, copper, etc., which will not burn in the air, burn in oxygen with ease.

#### ACTION OF OXYGEN AT HIGHER TEMPERATURES.

*Experiment 21.*—In a deflagrating-spoon set fire to a little sulphur and let it burn in the air. Notice whether it burns with ease or with difficulty. Notice the odor of the fumes which are given off. Now set fire to another small portion and introduce it in a spoon into one of the vessels containing oxygen, as shown in Fig. 9. It will be seen that the sulphur burns much more readily in the oxygen than in the air. Notice the odor of the fumes given off. Is it the same as that noticed when the burning takes place in the air?

*Experiment 22.*—Perform similar experiments with charcoal.

*Experiment 23.*—Burn a piece of phosphorus not larger than a small pea in the air and in oxygen. In the latter case the light emitted from the burning phosphorus is so intense that it is painful to some eyes to look at it. It is better to be cautious. The phenomenon is an extremely brilliant one. The walls of the vessel in which the burning takes place become covered with a white substance which afterwards gradually disappears.

*Experiment 24.*—Fasten a piece of iron picture-wire in a cap of metal, such as is used for fixing a deflagrating-spoon in an upright position, and dip the lower end in melted sulphur. Set fire to this and insert it into a vessel containing oxygen in which there is water to the depth of 3 or 4 inches to prevent the glass from breaking. For a moment the sulphur will burn as in Experiment 21; but soon the steel will begin to burn brilliantly, and the burning will continue as long as there is oxygen left in the vessel. Notice that in this case *there is no flame*, but instead very hot particles are given off from the burning iron. The phenomenon is of great beauty, especially if observed in a dark room. The walls of the vessel become covered with a dark reddish-brown substance, some of which will also be found at the bottom in

larger pieces. This substance is a compound of iron and oxygen known as magnetic oxide of iron.

**What has Taken Place?**—What has taken place in these experiments? The substances were simply heated before being introduced into the oxygen. Nothing was added to them except heat. It is clear that while oxygen does not act upon these substances at ordinary temperatures, it does act upon them at higher temperatures. But what does the action consist in? We can determine this only by a careful study of the substances before and after the action. We must know not only what substances are brought together, *but also what weight* of each; and we must know what substances are left behind, and the exact weights of these. In the cases mentioned it would be a difficult matter for one not thoroughly trained in the use of chemical methods to make all these determinations accurately, and unless they were made accurately they would fail to furnish the desired explanation. The determinations have fortunately been made so frequently that there can be no doubt as to what would be found were the experiments to be repeated, and for the present it will be necessary to accept the results, and use them as the basis of our reasoning. Something, however, may be learned with but little difficulty. If in the experiment with sulphur the spoon is examined after the burning stops, it will be found that the sulphur has disappeared. It will also be noticed that there is present an invisible \* substance which has a strong, disagreeable odor. This substance is not oxygen and it is not sulphur, but it is a gas that is formed by the burning of sulphur

\* The fumes first noticed subside if a little water is in the bottle.

in oxygen. What has become of the oxygen? That it is no longer present in its original condition may be shown by introducing a burning stick into the vessel. Instead of continuing to burn with increased activity, as it does in oxygen, it is extinguished.

In the experiment with carbon the results are similar, only the invisible substance has no odor.

In the experiment with phosphorus the white substance which is deposited on the walls of the vessel is not phosphorus, as is clear from the fact that it dissolves in water.

**Proof that the Oxygen Combines with the Burning Substance.**—The oxygen being invisible, it is more difficult to determine whether it enters into combination or not, but that it does can be shown by properly devised experiments. It is only necessary to burn a substance in a closed vessel containing oxygen, and to determine, after the burning, whether there is less oxygen than there was before. Lavoisier, who first showed what part the oxygen plays in burning, made a very important experiment much like the following: Some phosphorus is enclosed in a sealed tube with oxygen, and, by heating from without, the phosphorus is set on fire. After the action is over, one end of the tube is broken off under water, when water rushes in showing that the gas that was in the tube has disappeared. A modification of this experiment is here described.

**PROOF THAT THE OXYGEN COMBINES WITH THE BURNING  
SUBSTANCE.**

*Experiment 25.*—(T) Arrange an apparatus as shown in Fig. 10. *A* is a glass tube about 60 cm. (2 feet) long and about  $3\frac{1}{4}$  cm. ( $1\frac{1}{4}$  inches) in diameter. This is connected by means of a bent tube with the small flask *B*, of 50 to 100 ccm. capacity, which is fitted

with a stopper having two holes. This flask is carefully dried, and three layers of thin asbestos paper laid on the bottom inside, and upon this a thin layer of iron dust or fine iron filings or, better, freshly reduced "iron by hydrogen" (which see). The lower end of *A* is immersed to the extent of about 5 cm. (2 inches) in water. A current of oxygen is now passed through the apparatus by

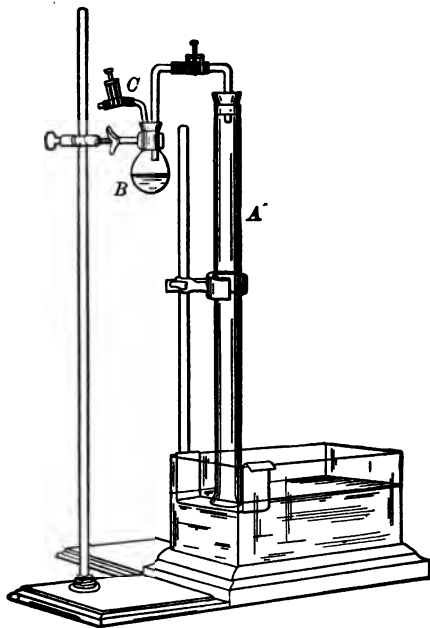


FIG. 10.

connecting at *C* with a gasometer. When the air has been displaced the current of oxygen is stopped, and the stop-cock at the end of *C* is closed. Now heat the flask gently. When the iron begins to glow, remove the flame.' What evidence is furnished that the oxygen enters into combination and disappears as a gas?

**Products Formed.**—Experiments of the kind described have shown that, whenever a substance burns in oxygen,



both the substance and the oxygen lose their characteristic properties, and that something else is formed in their place. In other words, the process is one of chemical combination. Sulphur combines with oxygen to form a gaseous product known as sulphur dioxide. It is this gas that gives the strong odor when sulphur burns. Carbon combines with oxygen to form the invisible gas carbon dioxide, commonly called carbonic acid gas. Phosphorus combines with oxygen to form a white solid, phosphorus pentoxide, which dissolves in the water present and disappears. All these products are well known, and they will be studied when the elements sulphur, carbon, and phosphorus are taken up.

**Proportions by Weight in which the Substances Combine with Oxygen.**—The next question that presents itself is this: In what proportions by weight do the substances combine with oxygen? Is there anything definite in these proportions, or do they combine in any possible proportions? This is a very important question, and it has given rise to a great deal of experimenting, especially in the early part of the last century. It is impossible to repeat these experiments here, but the method of work can be made clear by a general account. Suppose magnesium is taken for experiment. A small quantity is accurately weighed by a chemical balance. It is now heated in oxygen, and, after the action is complete, the product is weighed. The experiment is repeated a number of times, and all the weights are carefully recorded. If every precaution is taken to secure accuracy, it will be found that *these elements always combine in the same proportion by weight*: 1 gram of oxygen combines with  $1\frac{1}{2}$  grams of magnesium. By similar experiments it has been

shown that whenever carbon burns in oxygen these two elements combine in the same proportion by weight—1 gram of carbon combining with  $2\frac{3}{4}$  grams of oxygen; and similar results have been obtained in all other cases. This act of combining with oxygen is one involving the action of definite weights of substances.

**Relation of the Weight of the Product to the Weights of the Combining Substances.**—In the experiment with magnesium described in the preceding paragraph the oxygen was not weighed. The increase in the weight of the magnesium caused by combination with oxygen was determined, and the increase was ascribed to oxygen. A thoroughly satisfactory experiment would, however, involve the weighing of the magnesium, of the oxygen, and of the product formed. Such experiments have been made in great number, and it has been shown that the weight of the substance burned added to that of the oxygen used up is exactly equal to the weight of the substance formed.

**Burning in the Air.**—One cannot well help noticing a strong resemblance between the burning of substances in oxygen and in the air, and the question suggests itself, Are these two acts the same? The only way to answer this question is to burn the same things in pure oxygen and in air, and to see whether the same product is formed in each case, and whether anything else is formed. If this comparison should be made in any case, it would be found that whether a substance burns in the air or in pure oxygen the same product is formed, and nothing else. It is therefore certain that the act of burning in the air is due to the presence of oxygen. We shall learn later that the reason

why substances do not burn as readily in the air as in pure oxygen is that in the air there is present a large quantity of another gas that does not act upon the substances at all.

**Combustion.**—By the term combustion in its broadest sense is meant any chemical act that is accompanied by an evolution of heat. Ordinarily, however, it is restricted to the union of substances with oxygen in the way that this union takes place in the air, with evolution of light and heat. Substances which have the power to unite with oxygen are said to be *combustible*, and substances which have not this power are said to be *incombustible*. Most elements combine with oxygen under proper conditions, and are therefore combustible. Most compounds formed by the union of oxygen with combustible substances are incombustible. For example, the carbon dioxide and phosphorus pentoxide obtained in Experiments 22 and 23 are incombustible. They contain oxygen, and they cannot directly combine with any more.

**Kindling Temperature.**—We have seen that substances do not usually combine with oxygen at ordinary temperatures, but that in order to effect the union the temperature must be raised. If this were not the case, it is plain that every combustible substance in nature would burn up, for the air supplies a sufficient quantity of oxygen for this purpose. Some substances need to be heated to a high temperature before they will combine with oxygen; others require but very slight elevation. If we were to subject a piece of phosphorus, one of sulphur, and one of carbon to the same gradual rise in temperature, we should find that the phosphorus takes fire very easily, only a slight elevation of tem-

perature being necessary; next in order would come the sulphur; and last the carbon. If we were to repeat these experiments a number of times, we should find that the phosphorus would always take fire at the same temperature, and a similar result would be reached in the case of sulphur and carbon. Every combustible substance has its kindling temperature; that is, the temperature at which it will unite with free oxygen. Below this temperature it will not unite with oxygen except very slowly. If a piece of wood could be heated to its kindling temperature all at once, it would burn up as rapidly as it could secure the necessary oxygen; but the burning does not usually take place rapidly, for the reason that only a small part of it is at any one time heated to the kindling temperature. Watch a stick of wood burning, and see how, as we say, "the fire creeps" slowly along. The reason of the slow advance is simply this: only those parts of the stick that are nearest the burning part become heated to the kindling temperature.

**Slow Combustion or Slow Oxidation.**—Substances may combine slowly with oxygen without evolution of light. Thus, if a piece of iron is allowed to lie in moist air, it becomes covered with rust. This rust is similar to the substance formed when iron is burned in oxygen. Both are formed by the union of iron and oxygen. Magnesium burns in the air, as we have seen, and forms a white compound containing oxygen. It burns with increased brilliancy in oxygen, forming the same compound. If left in moist air for some days or weeks, it becomes covered with a layer of the same white substance. If this is scraped off and the magnesium is

further exposed, it will again become covered with a layer of the compound with oxygen, and this may be continued until the magnesium has been completely converted into the same substance that is formed when it burns in oxygen or in the air. Many other similar cases of slow oxidation might be described, some of which, such as the decay of wood, are constantly taking place in nature.

**Breathing.**—The most important illustration of slow oxidation is that which takes place in our bodies, for the food that we partake of undergoes a great many changes; some of the substances uniting with oxygen, and thus keeping up the temperature of our bodies. This, however, is done without evolution of light and without much evolution of heat. We take large quantities of oxygen into our lungs in breathing. This acts upon various substances presented to it, oxidizing them to other forms which can easily be got rid of. More will be said in regard to the breathing process of animals and plants when the subject of carbon and its compounds with oxygen is considered.

**Heat of Combustion.**—What is the chief difference between ordinary combustion and slow combustion? So far as we can judge by a cursory examination, it is that in the former light and heat are produced, while in the latter no light and very little or no heat is produced. Remembering that the reason why a body gives light is that it is heated to a sufficiently high temperature, the problem resolves itself into a question of heat. What difference, if any, is there between the quantity of heat given off when a substance burns and when it undergoes slow oxidation without evolution of light? The answer is of the highest importance.

*There is no difference whatever.* In the one case the heat is all given off in a short time, and therefore the temperature of the substance becomes high and it emits light. In the other the heat is evolved slowly and continues for a much longer time, and therefore the temperature of the substance is not markedly raised, as surrounding substances conduct off the heat as rapidly as it is evolved. If, however, we were to measure the *quantity* of the heat, we should find it to be the same in both cases.

**How the Quantity of Heat is Measured.**—The quantity of heat given off in a chemical reaction can be measured by allowing the reaction to take place in a vessel called a calorimeter, so constructed as to prevent loss of heat, and containing a known weight of water. The temperature of the water is noted at the beginning of the operation and at the end. A quantity of heat is generally stated by giving the number of grams of water which it will raise one degree (centigrade) in temperature. The quantity of heat necessary to raise the temperature of a gram of water from  $0^{\circ}$  to  $1^{\circ}$  (centigrade) is the unit used in heat-measurement. It is called the *calorie*. If, therefore, we say the quantity of heat evolved in any reaction is 250 calories (written generally 250 cal.), we mean simply a quantity of heat which would raise the temperature of 250 grams of water one degree (centigrade) in temperature.

To repeat, then: By the heat of combustion of a substance is meant the quantity of heat given off when a certain weight of the substance combines with oxygen.

It will be found that not only is the heat of combustion a fixed quantity whether the union with oxygen takes place

slowly or rapidly, but that the heat evolved in any given chemical reaction is always the same, and that chemical combination is always accompanied by an evolution of heat.

**Heat of Decomposition.**—Just as it is true that a definite quantity of heat is evolved when two or more elements combine chemically, so also it is true that in order to decompose the compound formed the same quantity of heat is required.

**Chemical Energy and Chemical Work.**—Any substance that has the power to unite with others can do *chemical work*,—it possesses *chemical energy*. Thus, all combustible substances can do work. In uniting with oxygen heat is evolved, and this can be transformed into motion. To go back to the example of the steam-engine, the cause of the motion is the burning of the fuel. It will thus be seen that the source of the power in the steam-engine is chemical energy. Substances that have not the power to combine with others have no power to do chemical work, or they have no chemical energy. As far as power to combine with oxygen is concerned, water is a substance of this kind, as is also carbon dioxide, the gas formed when carbon is burned in oxygen. In order that they may do work, they must first be decomposed and their constituents put together in some form in which they have the power of combination. This decomposition of carbon dioxide and water is taking place constantly on the earth. All plant-life is dependent on it. The products of the action, as, for example, the different kinds of wood, have energy,—they can do chemical work. This power to do work has been acquired from the heat of the sun, to which the decomposition of the carbon

dioxide and water is mainly due. There is thus a transformation of the sun's heat into chemical energy, which is stored up in the combustible wood. The quantity of heat that would be given off in burning the wood is exactly equal to the quantity used up in its formation.

**Oxides.**—The compounds of oxygen with other elements are called *oxides*. To distinguish between different oxides the name of the element with which the oxygen is in combination is prefixed. Thus the compound of zinc and oxygen is called zinc oxide; that of calcium and oxygen, calcium oxide; that of silver and oxygen, silver oxide, etc.

**Summary.**—Oxygen can be made by heating mercuric oxide, potassium chlorate, manganese dioxide, or a mixture of potassium chlorate and manganese dioxide; and by treating ozone with water.

The physical properties and the chemical properties of oxygen have been studied.

Oxygen does not readily act upon other substances at ordinary temperatures.

Oxygen acts readily upon many substances at higher temperatures.

Oxygen combines with many substances giving heat and light, and forming new substances. These acts of combination take place between definite quantities of the substances, and in any given case the weight of the product is equal to the weight of the substance that combines with the oxygen plus the weight of the oxygen used up.

Burning in the air is due to the combination of the burning substance with oxygen.



Kindling temperature is that temperature to which a substance must be heated before it will combine with oxygen.

Slow combustion and breathing are the same as ordinary combustion except that they take place so slowly that the temperature does not rise very much.

The quantity of heat produced by a given weight of a substance that burns in air or oxygen is the same in the end whether the burning is rapid or slow.

A substance is said to possess *chemical energy* if it has the power to combine with others. In combining with other substances or acting upon them *chemical work* is done.

The compounds of oxygen with other elements are called *oxides*.

**Practical Uses of Oxygen.**—Persons injured by inhaling illuminating gas or other poisonous gases, or so weakened by illness that they cannot inhale enough air to obtain the requisite oxygen, are helped by respiration of pure oxygen.

Technically, oxygen is used to obtain high temperatures, since combustible gases burn more rapidly in oxygen than in air. The *calorimetric* effect or total amount of heat obtained from a given weight of a combustible substance is the same whether the substance burns quickly or slowly. The *pyrometric* effect or temperature attained is proportional to the speed of combustion.

**Commercial Methods of Obtaining Oxygen.**—Large quantities of oxygen are now obtained by the electrolysis of dilute sodium hydroxide as by-product in the technical preparation of hydrogen. It is, however, chiefly obtained directly or indirectly from the air; directly by liquefying air

and allowing the nitrogen, which boils at  $-195.5^{\circ}$ , to boil off, leaving the oxygen, which has a higher boiling point, behind. Oxygen is obtained indirectly from the air by several methods. Brin's process depends on the fact that when barium oxide is heated in a current of air at  $550^{\circ}$  it absorbs oxygen from the air, forming barium dioxide, which at  $700^{\circ}$  gives off the oxygen absorbed from the air and is converted into barium oxide; thus alternate heating and cooling between these temperatures yields large quantities of oxygen.

In the actual process, the temperature is kept constant at  $700^{\circ}$ , while air *under pressure* is forced through the tubes containing the oxide, a valve at the end of the tube permitting the nitrogen to escape. When the first reaction is complete a partial vacuum is produced in the tubes and the second reaction occurs at the *reduced pressure* without changing the temperature, thus economizing time and fuel. The product obtained contains about 96% oxygen. It is compressed into steel cylinders with a pressure of 100 atmospheres. As the volume of a gas is inversely proportional to the pressure upon it, a cylinder of 10 liters capacity filled with oxygen under a pressure of 100 atmospheres yields 1000 liters of oxygen at atmospheric pressure.

## CHAPTER III.

### HYDROGEN.

IN Experiment 4 it was found that when an electric current is passed through water two gases are obtained, one of which has since been studied and found to be oxygen. The other, it will be remembered, takes fire and burns; and is thus easily distinguished from oxygen. This second gas is hydrogen.

**Occurrence.**—Hydrogen is found in nature very widely distributed, and in large quantity. It forms one ninth of the weight of water, and is contained in most substances that enter into the composition of plants and animals.

**Preparation of Hydrogen.**—It can be prepared:

- (a) By decomposition of water by means of the electric current (electrolysis of water);
  - (b) By decomposition of water by the action of certain metals;
  - (c) By the action of substances known as acids on metals.
- The following experiments will illustrate these methods.

#### HYDROGEN BY THE DECOMPOSITION OF WATER.

*Experiment 26.*—(T) Repeat Experiment 4 and examine the gases.

*Experiment 27.*—(T) Place a small piece of sodium \* on water.

\* The metals sodium and potassium are kept under oil. When a

While it is floating on the surface apply a lighted match to it. A yellow flame will appear. This is burning hydrogen, the flame being colored yellow by the presence of the sodium, some of which also burns. Make the same experiment with potassium. The flame appears in this case without the aid of the match. It has a violet color which is due to the burning of some of the potassium. The gas given off in these experiments is either burned at once or escapes into the air. In the case of the potassium the action takes place rapidly, and the heat evolved is sufficient to set fire to the gas. In the case of the sodium the heat evolved does not set fire to the gas. In order to collect it unburned, it is only necessary to allow the decomposition to take place, so that the gas will rise in an inverted vessel filled with water. For this purpose fill a good-sized test-tube with water and invert it in a vessel of water. Cut off a piece of sodium not larger than a pea, wrap it in a layer or two of filter-paper, and with the fingers or a pair of curved forceps bring it quickly below the mouth of the test-tube and let it go. It will rise to the top, the decomposition of the water will take place quietly, and the gas formed, being unable to escape, will remain in the tube. By repeating this operation in the same tube a second portion of gas may be made, and so on until enough has been collected.

Examine the gas and see whether it acts like the hydrogen obtained from water by means of the electric current. What evidence have you that they are the same? Is this evidence sufficient to prove the identity of the two? Examine the water on which the sodium or potassium has acted. Wet the fingers with it and rub them together. Taste the water. Does it change the color of red litmus paper?

**Action of Sodium and Potassium on Water.**—The explanation of the action of sodium and potassium on water will

small piece is wanted take out one of the larger pieces from the bottle, roughly wipe off the oil with filter-paper and cut off a piece the size needed. It is not advisable to use a piece larger than an ordinary pea.

be given later. Suffice it for the present to say that water consists of hydrogen and oxygen, and that when sodium comes in contact with it this element takes the place of some of the hydrogen, forming the compound sodium hydroxide or caustic soda. The action of potassium is of the same kind. The product is potassium hydroxide or caustic potash.

**Decomposition of Water by Iron.**—Some metals that do not decompose water at ordinary temperatures, or that decompose it slowly, do so easily at elevated temperatures. This is true of iron. If steam is passed through a tube containing pieces of iron heated to redness, decomposition of the water takes place, the oxygen is retained by the iron, which enters into combination with it, while the hydrogen is liberated.

#### HYDROGEN BY THE DECOMPOSITION OF WATER BY IRON.

*Experiment 28.*—(T) In this experiment a porcelain tube with an internal diameter of from 20 to 25 mm. (about an inch) and

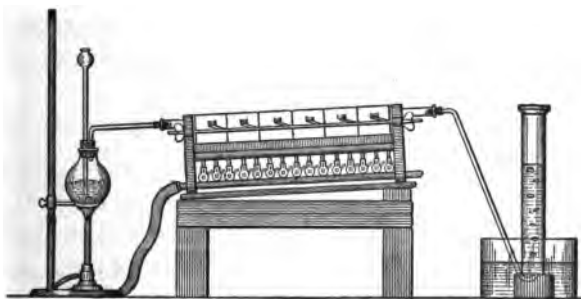


FIG. 11.

a gas-furnace are desirable, though a hard-glass tube and a charcoal-furnace will answer. The arrangement of the apparatus is shown in Fig. 11. The hydrogen can be collected by displace-

ment of water, as in the case of oxygen. The products formed are magnetic oxide of iron and hydrogen.

**Decomposition of Water by Carbon or Charcoal.**—Many other substances have the power to decompose water and set hydrogen free. The fact that a combustible gas can be obtained from water has led to many attempts to manufacture gas for heating and illuminating purposes from this substance. There is, however, no cheap substance that has the power to decompose water at ordinary temperatures. All practicable methods involve the use of heat, and it is not infrequently the case that the quantity of heat required to effect the decomposition is greater than that which can be obtained by burning the hydrogen formed. In the manufacture of the so-called "water-gas" which is now extensively used in the United States both for illuminating and heating purposes, water is decomposed by means of carbon in the form of hard coal. Two gaseous products are formed, both of which burn. They are carbon monoxide, or carbonic oxide, and hydrogen. This subject will be more fully discussed under the head of carbon monoxide.

**Action of Acids upon Metals.**—By far the most convenient method for making hydrogen consists in treating a metal with an acid. As will be seen later, acids are substances that contain hydrogen, and some of them are characterized by the fact that they give up this hydrogen easily and take up other elements in its place. The acids used in making hydrogen are *hydrochloric acid* and *sulphuric acid*. The chemistry of these compounds will be taken up in due time; but as we shall be obliged to use them before they

are studied systematically, a few words in regard to them are desirable at this time.

*Hydrochloric acid* is a compound of hydrogen and chlorine. It is a gas that dissolves easily in water. It is this solution that we use in the laboratory. It is manufactured in large quantities. It is sometimes called "muriatic acid."

*Sulphuric acid* is a compound of sulphur, oxygen, and hydrogen. It is a thick liquid. It is manufactured in very large quantities, as it plays an important part in many of the largest chemical industries.

When a metal, as zinc, is brought in contact with hydrochloric or sulphuric acid, an evolution of gas takes place at once.

#### HYDROGEN BY THE ACTION OF ACIDS ON METALS.

*Experiment 29.*—In a cylinder or test-tube put some small pieces of zinc, and pour upon it some ordinary hydrochloric acid. After the action has continued for a minute or two apply a lighted match to the mouth of the vessel. The gas will take fire and burn. If sulphuric acid diluted with five or six times its volume of water\* is used instead of hydrochloric acid, the same result will be reached. The gas evolved is hydrogen. For the purpose of collecting the gas the operation is best performed in a bottle with two necks called a Woulff flask (see Fig. 12), or in a wide-mouthed bottle in which is fitted a cork with two holes (see Fig. 13). Through one of the holes a funnel-tube passes, and through the other a glass tube bent in a convenient form.

\* If it is desired to dilute ordinary concentrated sulphuric acid with water, the acid should be poured slowly into the water while the mixture is constantly stirred. If the water is poured into the acid, the heat evolved at the place where the two come in contact may be so great as to convert the water into steam and cause the acid to spatter.

The zinc used is granulated. This is prepared by melting zinc in a ladle and pouring the molten metal from an elevation of four or five feet into water. The advantage of this form is that it presents a large surface to the action of the acids. A handful of this zinc is introduced into the bottle, and enough of a *cooled* mixture of sulphuric acid and water (1 volume concentrated acid to 6 volumes water) poured upon it to cover it. The reason for cooling the diluted acid is that hot acid causes too rapid action

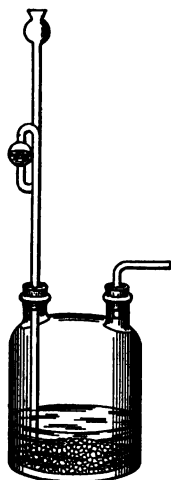


FIG. 12.

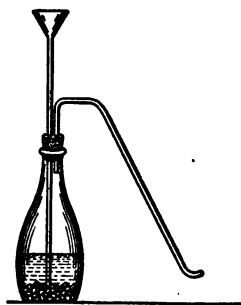


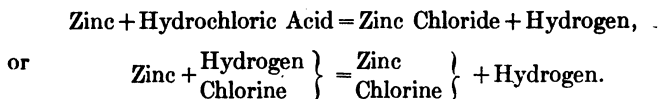
FIG. 13.

and at the higher temperature other products will be formed. Usually \* a brisk evolution of gas takes place at once. Let the gas escape for two or three minutes, and then collect some of it by displacement of water. When the action becomes slow, add more of the dilute acid. It will be well to fill several cylinders and bottles with the gas, and also a gasometer, from which it can be taken as it is needed for the experiments described below.

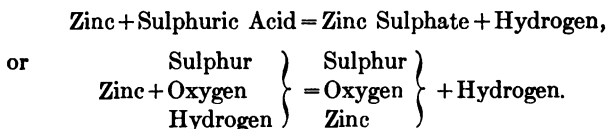
\* If action takes place slowly, pour in a little of a solution of copper sulphate.



When zinc acts upon hydrochloric acid it takes the place of the hydrogen in the hydrochloric acid and forms the compound zinc chloride:



When zinc acts upon sulphuric acid, it takes the place of the hydrogen and forms the compound zinc sulphate:



#### KIPP'S APPARATUS.

For making hydrogen as well as other gases Kipp's apparatus is often convenient. It is made up as shown in Fig. 13a. The lower part consists of the vessel A B;

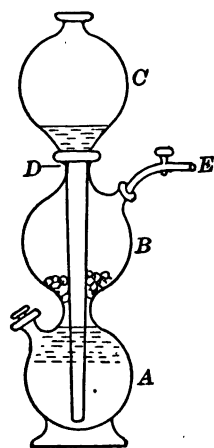


FIG. 13a.

the upper part C is a funnel the tube of which reaches down nearly to the bottom of A. B and C are connected by a ground glass joint at D. The substance from which the gas is to be evolved is put in B. The acid that is to act upon B is poured into C, the stop-cocks in A and B having previously been closed. When the stop-cock of B is opened the acid runs down into A, and rises until it comes in contact with the substance in B. Gas is evolved and, after driving the air out of B, escapes from the tube at E. If no more gas is needed the stop-

cock of the tube in B is closed. The gas not being able to escape presses the acid out of B and soon the action ceases.

In making hydrogen zinc and dilute sulphuric acid are used in this apparatus.

It is essential that the substance in B, the zinc, for example, in the case of hydrogen, should be in pieces large enough to prevent its passing into the lower vessel A. A powder cannot be used successfully with this apparatus. Sometimes the substance to be acted upon is mixed with gypsum and made into cubes of proper size. The gypsum is not acted upon by the acid.

#### FORMATION OF ZINC SULPHATE.

*Experiment 30.*—After Experiments 31–36 have been performed pour the contents of the flask in which the hydrogen has been generated through a filter into an evaporating dish, and boil off the greater part of the water, so that, on cooling, some of the substance contained in solution will be deposited. If the operation is carried on properly, the substance will be deposited in regular forms called crystals. It is zinc sulphate.

**Physical Properties of Hydrogen.**—Hydrogen is a colorless, inodorous, tasteless gas. Made by the action of zinc on acids, it has a slightly disagreeable odor. This is due to the presence of impurities. If it is passed through certain substances that have the power to destroy the impurities, the odor is destroyed.

#### PURIFICATION OF HYDROGEN.

*Experiment 31.*—Pass some of the gas through a wash-cylinder containing a solution of *potassium permanganate*; collect some of it, and notice whether it has an odor. The apparatus should be arranged as shown in Fig. 14. The solution of potassium

permanganate is, of course, contained in the small cylinder *A*, and the tubes are so arranged that the gas bubbles through it.

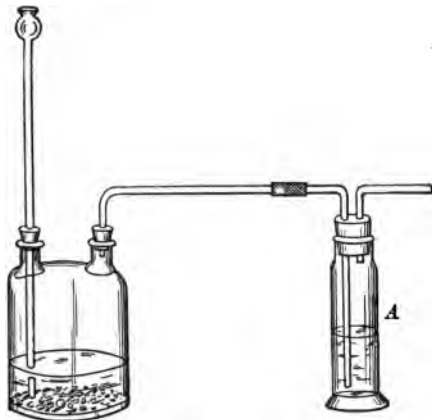


FIG. 14.

The gas is not poisonous. We could not, however, live in an atmosphere of hydrogen, as oxygen is essential to life. It is the lightest known substance, being very nearly fourteen and a half times lighter than the air and sixteen times lighter than oxygen. Its lightness may be shown by a number of simple experiments.

#### LIGHTNESS OF HYDROGEN.

*Experiment 32.*—Place a vessel containing hydrogen with the mouth upward and uncovered. In a short time examine the gas, and see whether it is hydrogen.

*Experiment 33.*—Gradually bring a vessel containing hydrogen with its mouth upward below an inverted vessel containing air, in the way shown in Fig. 15. The air will be displaced. On examination the inverted vessel will be found to



FIG. 15.

contain hydrogen, while the one with the mouth upward will contain none. The gas is thus poured upwards.

*Experiment 34.*—Soap-bubbles filled with hydrogen rise in the air. This experiment is best performed by connecting an ordinary clay pipe by means of a piece of rubber tubing with the exit tube of a gasometer filled with hydrogen. Small balloons of collodion are also made for the purpose of showing the lightness of hydrogen.

Balloons are always filled with hydrogen, or some other light gas. Some kinds of illuminating-gas are rich in hydrogen, and may therefore be used for the purpose.

A litre of hydrogen at  $0^{\circ}$  (centigrade), and under the pressure of 760 mm. (mercury), weighs 0.08995 gram. Its specific gravity is 0.0696. A comparison of these figures with the corresponding figures for oxygen leads to an interesting observation. The weight of a litre of oxygen is 1.429 grams; its specific gravity is 1.1056. The ratio of the weights of equal volumes of hydrogen and oxygen to each other is very nearly 1:16, or

$$0.08995:1.429::1:\text{nearly } 16.$$

At a very low temperature and high pressure, it can be converted into a liquid that boils at  $-252^{\circ}$ . By evaporating liquid hydrogen in a vacuum very low temperatures are reached and the hydrogen freezes, forming white crystals which melt at  $-258.9^{\circ}$ . It cannot be liquefied at any temperature above  $-242^{\circ}$ , no matter what pressure it may be subjected to.

**Critical Points.**—There is a definite temperature for every gas, above which no amount of pressure liquefies it. This is called its *critical temperature*. The critical temperature of hydrogen is  $-242^{\circ}$ , of oxygen  $-118^{\circ}$ , of car-

bon dioxide  $31^{\circ}.35$ , of ammonia  $130^{\circ}$ . The pressure required to liquefy a gas at its critical temperature is called its *critical pressure*. Data like these, the boiling-points of liquids, melting-points of solids, and the like, which are independent of the chemical behavior of the substance, are called *physical constants*.

**Chemical Properties of Hydrogen.**—Under ordinary circumstances, hydrogen is not a particularly active element, It does not unite with oxygen at ordinary temperatures, but, like wood and most other combustible substances, it must be heated to the kindling temperature before it will burn. We have seen that it burns when a flame is applied to it. The flame of burning hydrogen is colorless, or slightly blue. As burned under ordinary circumstances, the flame is colored in consequence of the presence of foreign substances; but that it is colorless when the gas is burned alone can be shown by burning it from a platinum tube, which is itself not acted upon by the heat.

**THE FLAME OF BURNING HYDROGEN IS COLORLESS.**

*Experiment 35.*—(T) If there is no small platinum tube available, roll up a small piece of platinum foil and melt it into the end of a glass tube, as shown in Fig. 16. Connect the burner thus made with the gasometer containing hydrogen, and after the gas has been allowed to issue from it for a moment, set fire to it. In a short time it will be seen that the flame is practically colorless and gives no light. That it is hot can be shown by holding a piece of platinum wire or a piece of some other metal in it.

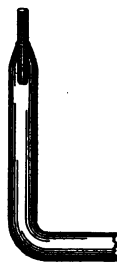


FIG. 16.

Hydrogen burns. We have seen that what is called burning consists in combining with oxygen.

On the other hand, substances that burn in the air are extinguished when put into a vessel containing hydrogen. This is equivalent to saying that a substance that is uniting with oxygen does not continue to unite with oxygen when put in an atmosphere of hydrogen, and does not combine with the hydrogen. This is expressed by saying that hydrogen does not support combustion. The following experiment shows this.

#### HYDROGEN DOES NOT SUPPORT COMBUSTION.

*Experiment 36.*—Hold a cylinder filled with hydrogen with the mouth downward. Insert into the vessel a lighted taper fixed on a bent wire, as shown in Fig. 17. The gas will take fire at the mouth of the vessel, but the taper will be extinguished. On withdrawing the taper and holding the wax for a moment in the burning hydrogen, it will take fire, but on putting it back in the hydrogen it will again be extinguished. Other burning substances should be tried in a similar way.

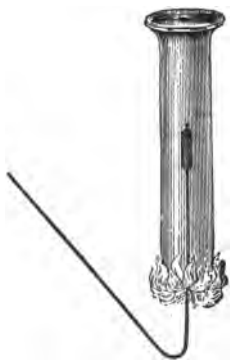


FIG. 17.

**Product Formed when Hydrogen Burns in Oxygen.**—As when hydrogen burns it combines with oxygen, a product should be obtained in which both hydrogen and oxygen are present. In the experiments performed we have seen no evidence of the formation of such a product, simply for the reason that when formed it is an invisible gas, and, though

it can easily be condensed to a liquid, no precautions were taken to get it in this form. The product is, in fact, ordinary water, which we shall next study.

**Technical Uses and Preparation of Hydrogen.**—Hydrogen is used technically for filling balloons, and to a limited extent as fuel when very high temperatures are desired. It is prepared technically by the electrolysis of a dilute water solution of sodium hydroxide, and is stored like illuminating gas in gasometers or is compressed into portable steel cylinders at 100–150 atmospheres pressure. Hydrogen is also prepared, though less economically, by dipping baskets containing scrap aluminium into dilute sodium hydroxide.

## CHAPTER IV.

### COMBINATION OF HYDROGEN AND OXYGEN.—WATER.

WATER was regarded as an element until, towards the end of the eighteenth century, the discovery of hydrogen and oxygen, and of the nature of combustion, led to the discovery of its composition.

**Occurrence.**—The wide distribution of water on the earth is familiar to every one. But water also occurs in forms and conditions which prevent its immediate recognition. Thus all living things contain a large proportion of water, that can be driven off by heat. If a piece of wood or a piece of meat is gently heated, water passes off.

#### OCCURRENCE OF WATER.

*Experiment 37.*—In a dry tube gently heat a small piece of wood. What evidence do you obtain that water is given off? Do the same thing with a piece of fresh meat.

2 The proportion of water in animal and vegetable substances is very great. If the body of a man weighing 150 pounds should be put in an oven and thoroughly dried, there would be left only about 40 pounds of solid matter, all the rest being water. As all meat, vegetables, and food-stuffs in general contain a similarly large proportion of water, it is evident that water is an important article of



commerce. When we buy four pounds of beef, we pay for about three pounds of water and one of solid matter.

**Water of Crystallization.**—Water also occurs in another form in which it does not easily reveal its presence. This is as *water of crystallization*.

#### WATER OF CRYSTALLIZATION.

*Experiment 38.*—Take some of the crystals of zinc sulphate obtained in Experiment 30. Spread them out on a layer of filter-paper, and finally press two or three of them between folds of the paper. Examine them carefully. They appear to be quite dry, and in the ordinary sense they are dry. Put them into a dry test-tube, and heat them gently. What evidence do you obtain of the giving off of water? Describe the changes which the crystals undergo.

*Experiment 39.*—Perform a similar experiment with some gypsum, which is the natural substance from which “plaster of Paris” is made.

*Experiment 40.*—Heat a few small crystals of copper sulphate or blue vitriol. What evidence of water? Describe the changes in the crystals. After no further change takes place, dissolve what is left in a little water. What is the color of the solution? Evaporate to the point of crystallization. How do the crystals obtained compare with those first taken?

Many compounds when deposited from solutions in water in the form of crystals are combined with definite quantities of water. This water is not present as such, but is held in chemical combination. Hence the substance does not appear moist, though it may contain more than half its weight of water. This water of crystallization is, in some way which we do not understand, essential to the form of the crystal. If it is driven off by heat, the crystal falls to pieces. Some compounds combine under different

circumstances with different quantities of water, the form of the crystals varying with the quantity of water in combination.

**Efflorescence.**—Compounds differ greatly as regards the ease with which they give up water of crystallization. In general, it is given off when the compound containing it is heated to the temperature of boiling water. But some compounds give it up when allowed to lie in the air. This is true of sodium sulphate, or Glauber's salt, which contains about 56 per cent of water of crystallization.

#### EFFLORESCENT COMPOUNDS.

*Experiment 41.*—Select a few crystals of sodium sulphate which have not lost their lustre. Put them on a watch-glass, and let them lie exposed to the air for an hour or two. What change takes place in their appearance? How does this change compare with that of the crystals of zinc sulphate?

Compounds which lose their water of crystallization by simple exposure to the air are said to *effloresce*. They are called *efflorescent*.

**Deliquescence.**—Some compounds if deprived of their water of crystallization will take it up again when allowed to lie in an atmosphere containing moisture. As the air always contains moisture, it is only necessary to expose such compounds to the air in order to show the phenomenon. It is well shown by the compound calcium chloride. This substance has a remarkable power of attracting water to itself and dissolving in it.

#### DELIQUESCENT COMPOUNDS.

*Experiment 42.*—Expose a few pieces of calcium chloride to the air for some hours. Describe the changes that take place.

Substances that absorb water from the air and dissolve in this water are said to *deliquesce*. They are called *deliquescent*.

**Analysis and Synthesis.**—In order to determine the composition of water, or of any other compound, we must analyze it. We may simply determine what substances enter into its composition without determining the relative quantities of these substances. In this case we make what is called a *qualitative analysis*. If, however, we not only determine what substances are present, but also in what proportion they are present, we then make a *quantitative analysis*.

The composition of a substance may also be determined by putting together its constituents and causing them to combine chemically. An operation of this kind is called a *synthesis*. A synthesis, then, is the opposite of an analysis. Just as we may make a qualitative or a quantitative analysis, so also we may make a *qualitative* or a *quantitative synthesis*. These processes are well illustrated by the operations necessary to determine the composition of water.

**Decomposition of Water by the Electric Current (Electrolysis of Water) and what it Teaches.**—That water contains hydrogen and oxygen has already been shown in Experiment 4. It will now be well to repeat the experiment and see whether we can learn anything more regarding the composition of water than that it contains hydrogen and oxygen. In the first place, the question suggests itself, In what proportions, by weight and by volume, are the gases combined?

## HYDROGEN AND OXYGEN IN WATER.

*Experiment 43.*—(T) The tubes in the apparatus used in Experiment 4, or some other similar apparatus, should be marked by means of a file, or by etching, so that equal divisions can be recognized. Tubes thus divided so that the divisions indicate cubic centimetres are most convenient for the purpose. Let the gases formed by the action of the electric current, as in Experiment 4, rise in the graduated tubes, and observe the volumes. It will be seen that when one tube is just full of gas, the other, if it is of the same size, will be only half full. On examining the gases the larger volume will be found to be hydrogen, and the smaller volume oxygen. This experiment has been performed an untold number of times and always with the same result.

The relative weights of equal volumes of the two gases are known, so that the relative weights of the gases obtained from water by the action of the electric current can easily be calculated. The ratio of the weights of equal volumes of hydrogen and oxygen is very nearly 1:16. Therefore, if two volumes of hydrogen are combined with one volume of oxygen, the ratio between the weights is 2:16 or 1:8. Although the above experiment shows that hydrogen and oxygen are obtained from water in the proportion of two volumes of the former to one of the latter, or of one part by weight of the former to nearly eight parts by weight of the latter, the experiment does not prove that this is the actual composition of water. For it may be that other elements besides hydrogen and oxygen are contained in the water, and it may be that all the hydrogen and oxygen are not set free by the action of the electric current. Whether either of these possibilities is true might be determined by decomposing a weighed quantity of water, and weighing the hydrogen and oxygen obtained from it. If

it should be found that the sum of the weights of hydrogen and oxygen is equal to the weight of the water decomposed, this fact would be conclusive evidence that only hydrogen and oxygen are contained in water, and that they are present in the proportions stated.

**Synthesis of Water by Burning Hydrogen.**—That water consists of hydrogen and oxygen only can be satisfactorily proved by effecting its synthesis. In the first place, it can be shown that water is formed when hydrogen burns in the air, and, as it has been shown that burning is combining with oxygen, the conclusion is justified that water consists of hydrogen and oxygen.

#### WATER PRODUCED BY THE BURNING OF HYDROGEN IN THE AIR

*Experiment 44.*—Pass hydrogen from a generating-flask or a gasometer through a tube containing some substance that will

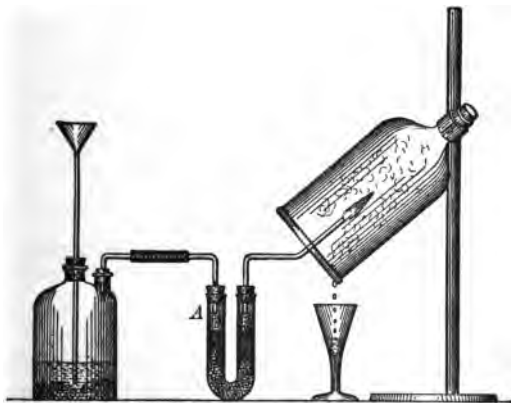


FIG. 18.

absorb moisture, for all gases made in the ordinary way and collected over water are charged with moisture. We have seen in

Experiment 42 (page 60) that calcium chloride has the power to absorb moisture. It is extensively used in the laboratory for the purpose of drying gases, and it may be used in the present experiment. It should be in granulated form, not powdered. After passing the hydrogen through the calcium chloride, pass it through a tube ending in a narrow opening, and set fire to it. If now a *dry* vessel is held over the flame, drops of water will condense on its surface and run down. A convenient arrangement of the apparatus is shown in Fig. 18.

A is the calcium chloride tube. Before lighting the jet hold a glass plate in the escaping gas, and see whether water is deposited on it. Light the jet *before* putting it under the bell-jar, otherwise if hydrogen is allowed to escape into the vessel it will contain a mixture of air and hydrogen, and this mixture, as will soon be seen, is explosive.

#### Synthesis of Water by Mixing Hydrogen and Oxygen.—

If hydrogen and oxygen are mixed together, and the mixture is allowed to stand unmolested, it remains unchanged. If, however, a spark or a flame is brought in contact with the mixture, a violent explosion occurs, and a careful examination has shown that the explosion is the result of the combination of the two gases. The noise is caused by the sudden contraction of the gases due to the combination and by the expansion which instantly follows in consequence of the evolution of heat.

#### ELECTROLYTIC GAS.

*Experiment 45.*—(T) Mix hydrogen and oxygen in the proportion of about 2 volumes of hydrogen to 1 volume of oxygen in a gasometer. Fill soap-bubbles, as directed in Experiment 34, with this mixture and allow them to rise in the air. As they rise bring a lighted taper in contact with them, when a sharp explosion will occur. Great care must be taken to keep all flames away from the vicinity of the gasometer and the end of the delivery-

tube. This experiment may be conveniently performed by hanging up, about six to eight feet above the experiment-table, a good-sized tin funnel-shaped vessel with the mouth downward. Now place a gas-jet or a small flame of any kind at the mouth of the vessel. If the soap-bubbles are allowed to rise below this apparatus they will come in contact with the flame and explode at once.\*

This experiment simply shows that a mixture of hydrogen and oxygen explodes when brought in contact with a flame, and that the gases do not act upon each other at ordinary temperatures.

**Quantitative Synthesis of Water.**—In order to show that when the explosion occurs water is formed, and in what proportions the gases combine, it is necessary to work in closed vessels so constructed as to permit accurate measurement of the volumes of the gases. The vessel in which the gases are brought together and caused to combine is called a *eudiometer* (from *ευδία*, calm air, and *μέτρον*, a measure). It is simply a tube graduated in millimetres and having two small platinum wires passed through it at the closed end, nearly meeting inside and ending in loops outside, as shown in Fig. 19. The eudiometer is filled with mercury, inverted



FIG. 19.

in a mercury trough, and held in an upright position by means of proper clamps. A quantity of pure hydrogen is passed up into the tube and its volume accurately measured.

\* The same apparatus may be used in experimenting with soap-bubbles filled with hydrogen.

About half this volume of oxygen is then introduced and accurately measured, and after the mixture has been allowed to stand for a few minutes, a spark is passed between the wires in the eudiometer by connecting the loops with the poles of a small Ruhmkorff coil or with a Leyden jar. Under these circumstances the explosion takes place noiselessly and with very little danger. If the interior of the tube was dry before the explosion, it will be seen to be moist afterwards, and a marked decrease in the volume of the gases is also observed. That water is the product of the action has been proved beyond any possibility of a doubt, over and over again. As the liquid water which is formed occupies an inappreciable volume as compared with the volume of the gases which combine, the decrease in volume represents the total volume of hydrogen and oxygen which have combined. Now, if the experiment is performed with the two gases in different proportions, it will be found that only when they are mixed in the proportion of two volumes of hydrogen and one volume of oxygen do they completely disappear in the explosion. If hydrogen is present in larger proportion, the excess is left over. If oxygen is present in larger proportion, the excess of oxygen is left over. It appears, therefore, that when hydrogen and oxygen combine to form water, they do so in the proportion of two volumes of hydrogen to one volume of oxygen.

**Synthesis of Water by Passing Hydrogen over Heated Oxides.**—The synthesis of water can be effected by passing hydrogen over a compound containing oxygen and heated to a sufficiently high temperature. A convenient substance for this purpose is the compound of copper and oxygen



known as copper oxide or black oxide of copper. When hydrogen is passed over this compound at ordinary temperatures no action takes place. If, however, the temperature is raised to low redness the hydrogen combines with the oxygen, forming water, and the copper is left behind as such.

#### ACTION OF HYDROGEN ON HOT COPPER OXIDE.

*Experiment 46.*—Arrange an apparatus as shown in Fig. 20. *A* is a Woulff flask for generating hydrogen. To remove impurities the gas is passed through a solution of potassium per-

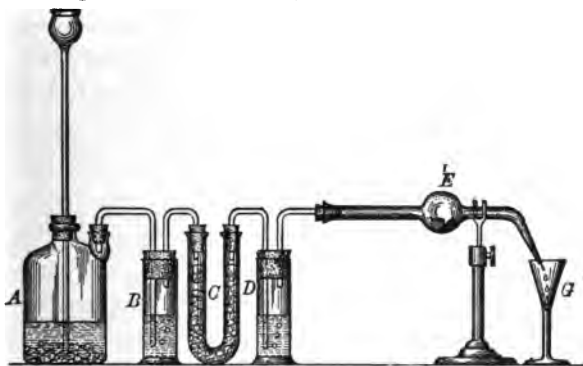


FIG. 20.

manganate contained in the wash-cylinder *B*. The U-tube *C* contains granulated calcium chloride, and the cylinder *D* contains concentrated sulphuric acid, both of them serving to remove moisture from the gas. The pure dry hydrogen is now passed through the hard-glass tube *E*, which contains a layer of copper oxide. After the apparatus is filled with hydrogen the copper oxide is heated to low redness by means of a small gas-jet. What evidence do you obtain of the formation of water? What change takes place in the color of the substance in the tube? Try the action of nitric acid on a little of the black oxide of copper, and on the substance left after the action of the hydrogen.

**Quantitative Synthesis of Water.**—In this case the loss in weight of the copper oxide represents oxygen. If, therefore, we should weigh the copper oxide before the experiment, and afterwards the copper, and should also collect and weigh the water formed, we could from the figures obtained readily calculate the relative weight of the oxygen contained in the water. The water can easily be collected by passing it into a tube filled with calcium chloride. If the tube is weighed before the experiment and after it, the gain in weight will represent the weight of the water collected. All these weighings can be made without difficulty on a chemical balance such as is found in every chemical laboratory. Where time and the equipment of the laboratory will permit it will be well for each student to carry out this experiment. A few experiments of this kind are of special importance for the reason that they serve to impress upon the mind the reality of the quantitative relations about which the student is constantly hearing. If it is performed, a small hard-glass tube from 12 to 15 centimetres (5 to 6 inches) long and about 1 centimetre (about half an inch) internal diameter should be used in place of the tube *E* in the qualitative experiment above described. The tube is drawn out at one end and a small plug of asbestos put in the small end. Connection with the weighed calcium-chloride tube is made at this end. The tube is first thoroughly dried. Then coarsely granulated copper oxide (a few grams) is introduced into it and the whole weighed. After the experiment the tube and the copper are weighed again. The calcium-chloride tube should of course be weighed before and after the experiment to get the weight of the water formed. The results are calculated thus:

Let  $x$  = weight of tube + copper oxide before the experiment;

$y$  = weight of tube + copper after the experiment.

Then  $x - y$  = weight of oxygen taken from the copper oxide.

Let  $a$  = weight of calcium-chloride tube before;

$b$  = " " " " " after.

Then  $b - a$  = weight of water formed.

If the experiment is carefully performed, it will be found that the ratio  $\frac{x-y}{b-a}$  is very nearly  $\frac{8}{9}$ .

**Oxidation and Reduction.**—Any substance which like hydrogen has the power to abstract oxygen from compounds containing it is called a *reducing agent*. The process of abstracting oxygen from a compound is called *reduction*. *Reduction* and *oxidation* are therefore complementary processes.

**The Oxyhydrogen Blowpipe.**—The heat evolved when hydrogen combines with oxygen is very great, and it is utilized for various purposes. To burn hydrogen in the air is, as we have seen, a simple matter, but to burn it in

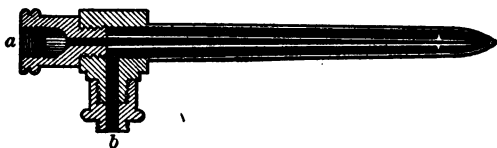


FIG. 21.

oxygen requires a special apparatus to prevent the mixing of the gases before they reach the end of the tube where the combustion takes place. The *oxyhydrogen blowpipe* answers this purpose. It is a tube with a smaller tube passing through it, as shown in Fig. 21.

The oxygen is admitted through *a*, and the hydrogen through *b*. It will be seen that they come together only at the end of the tube. The hydrogen is first passed through and lighted; then the oxygen is passed through slowly, the pressure being increased until the flame appears thin and straight. It gives very little light, but is intensely hot.

#### OXYHYDROGEN BLOWPIPE.

*Experiment 47.*—(T) Hold in the flame of the oxyhydrogen blowpipe successively a piece of iron wire, a piece of a steel watch-spring, a piece of copper wire, a piece of zinc, a piece of platinum wire.

Platinum vessels are used for many purposes, particularly for chemical operations. The vessels are made from molten platinum, the metal being melted by means of the oxyhydrogen blowpipe.

**The Lime-light.**—When the flame of the oxyhydrogen blowpipe is allowed to play upon some substance which it cannot melt nor burn up, the substance becomes heated so high that it gives off an intense light. The substance commonly used is quicklime. Hence the light is often called the lime-light. It is also known as the Drummond light.

#### THE LIME-LIGHT.

*Experiment 48.*—(T) Cut a piece of lime of convenient size and shape, say 25 mm. (1 inch) long by 20 mm. ( $\frac{3}{4}$  inch) wide, and the same thickness. Fix it in position so that the flame of the oxyhydrogen blowpipe will play upon it. The light is very bright, but by no means as intense as the electric light.

**Natural Waters.**—The purest water found in nature is rain-water, particularly that which falls after it has rained

for some time. That which first falls always contains impurities from the air. As soon as the rain-water comes in contact with the earth, and starts on its course toward the ocean, it begins to take up various substances, according to the character of the soil with which it comes in contact. Mountain streams that flow over rocky beds, particularly over beds of sandstone, which is very insoluble, contain exceptionally pure water. Streams that flow over limestone dissolve some of the stone, and the water becomes "hard." The many varieties of mineral springs have their origin in the presence in the earth of certain substances that are soluble in water. Common salt occurs in large quantities in different parts of the earth. As it is easily soluble in water, many streams contain it; and as all the streams find their way into the ocean, we see one reason why the water of the ocean should be salt. As streams approach the habitations of man they are subjected to a serious cause of contamination. The drainage from the neighborhood of human dwellings is apt to find its way into a near stream. This condition of things is most strikingly illustrated in the case of a large town situated on the banks of a river. It often happens that the water of the river is used for drinking purposes, and it also often happens that the water is contaminated by drainage. Water when once contaminated by drainage tends to become pure again by contact with the air. If it is to be used for drinking purposes, however, it is not well to rely too much upon this process of purification.

**Testing of Drinking-water.**—There is no simple process by which the value of a water for drinking purposes can

be determined in doubtful cases. Any marked odor, color, or taste furnishes good ground for suspicion. But many waters that are inodorous, colorless, and tasteless are not fit for use. In case of doubt a water should be submitted to a skilled chemist. Any examination made by an amateur is of practically no value.

**Distillation of Water.**—In order to get pure water, it must be distilled. Distillation consists in boiling the water, and then condensing the vapor by passing it through a tube which is kept cool by surrounding it with cold water. A simple apparatus for the purpose is that illustrated in Fig. 22.

The water to be distilled is placed in the flask *A*. The flask is connected by means of a bent glass tube *B* with

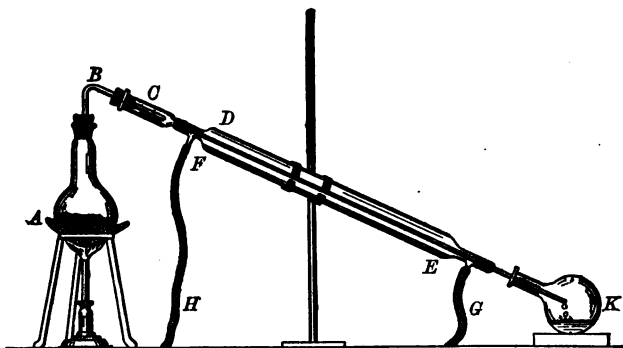


FIG. 22.

the long tube *CC*. This in turn is surrounded by the larger tube or jacket *D*. The side tube *E* is connected with a faucet by means of the rubber tube *G*. The water is allowed to flow slowly into the jacket and out at *F*, whence it passes through the rubber tube *H* to the sink. When the water

in *A* is boiled, the vapor passes into the tube *CC*. Here it is cooled and takes the form of liquid, which runs down and collects in the flask *K*, which is called the receiver.

#### DISTILLATION OF WATER.

*Experiment 49.*—Dissolve some copper sulphate, or other colored substance, in a litre of water, and distil the water.

**Properties of Water.**—Pure water is tasteless and inodorous. In thin layers it is colorless, but in thick layers it is blue. This has been shown in the laboratory by filling a long tube with distilled water. When looked through it appears blue. The beautiful blue color of the water of some lakes is the natural color of pure water.

On cooling, water contracts until it reaches the temperature  $4^{\circ}$ . At this point it has its maximum density. When cooled below  $4^{\circ}$  it expands, and the specific gravity of ice is somewhat less than that of water. Hence ice floats on water. If this were not so, in cold climates the water in the streams would freeze solid. As it is, the lower layers of water are protected by the ice and the cold water just below it, which are poor conductors of heat. This expansion of water on freezing is the cause of the constant disintegration or "weathering" of rock through water freezing in the crevices. On the weathering of rock depends largely the fertility of soil.

**Heat of Vaporization of Water and Heat of Fusion of Ice.**—These names are given to the heat required to change water into steam and ice into water respectively.

To heat 1 gram ice at	$0^{\circ}$	to form 1 gram water at	$0^{\circ}$	requires	80 cal.
" 1 " water at	$0^{\circ}$	" 1 " " "	$100^{\circ}$	"	100 "
" 1 " " at	$100^{\circ}$	" 1 " steam at	$100^{\circ}$	"	540.4 "
From ice to steam, 720.4 "					

The importance of these facts is evident when we consider what it would mean if great bodies of ice melted suddenly, or if a liter of water at  $100^{\circ}$  passed suddenly into steam, thereby increasing its volume to nearly 1700 liters. The enormous waste of energy in burning coal to heat water to form steam for steam power is also shown by these figures, as is conversely the efficiency of a steam jet for heating, as one gram steam at  $100^{\circ}$  in condensing to 1 gram water at  $100^{\circ}$  gives off 540.4 cal. This figure is the *heat of condensation of steam*.

**Water as a Solvent.**—It is known that many solids, liquids, and gases when brought into water disappear and form colorless liquids that look like water. Some give colored liquids of the same color as the substance dissolved, and others give liquids that have colors quite different from the dissolved substances. On the other hand there are many substances that do not dissolve in water. If a very small quantity of substance is dissolved in a large quantity of water, and the solution thoroughly stirred, the dissolved substance is uniformly distributed throughout the liquid, as can be shown by refined chemical methods. That the dissolved substance is everywhere present in the solution can be shown, further, by the aid of certain dye-stuffs, as, for example, magenta. A drop of a concentrated solution of this substance brought into many gallons of water imparts a distinct color to all parts of the liquid. An experiment of this kind gives some idea of the extent to which the subdivision of matter can be carried. For it is evident that in each drop of the dilute solution some of the coloring-matter must be contained, though the quantity



must be what we should call infinitesimal. While there seems to be no limit to the extent to which a solution can be diluted, and still retain the dissolved substance uniformly distributed through its mass, there is a limit to the amount of every substance that can be brought into solution, and this varies with the temperature, and, in the case of gases, with the pressure. Some substances are easily soluble; others are difficultly soluble. When the solutions are boiled the water simply passes off and leaves the dissolved substance behind, if it is a non-volatile solid. If, however, the substance in solution is a liquid a partial separation will take place, the extent of the separation depending largely upon the difference between the boiling-points of the water and the other liquid. If, finally, the substance in solution is a gas, it generally passes off when the solution is heated, though in some cases water is given off, leaving the gas or a compound of gas with water in solution.\*

**Ozone.**—When electric sparks are passed for a time through oxygen the gas undergoes a remarkable change. It acquires a strong odor, and is much more active than under ordinary circumstances. The odor of the gas thus formed is observed in the neighborhood of an electric machine in action, and is said to be noticed during thunder-storms. The substance that has the odor is ozone. It is formed in a number of chemical reactions, as when phosphorus acts on the air in the presence of water. By cold and pressure it has been changed to a dark-blue liquid.

\*The subject of solution will be more fully dealt with in Chapter VIII.

Ozone oxidizes many organic compounds energetically, hence it is now prepared commercially, for disinfection, bleaching, purification of water, and manufacture of dextrin. Ozone changes oxidizable substances into their highest oxides. Silver is changed to silver peroxide, phosphorus to phosphorus pentoxide, ammonia to ammonium nitrate, etc.

When a certain volume of oxygen is converted into ozone a contraction takes place. Three volumes of oxygen form two of ozone.

By heating ozone above  $300^{\circ}$  it is converted into ordinary oxygen, and two volumes of ozone give three of oxygen.

It is clear that the element oxygen can be converted into something else without the addition of any substance to it. This might lead us to conclude that oxygen is not an element. But the substance formed from it has exactly the same weight and can be changed back again to oxygen without any substance being added to it or taken from it. It follows that the change must take place within the oxygen itself. The commonly accepted explanation of the relation between oxygen and ozone cannot be given here but will be given later.

Ozone is present in small quantity in the air.

**Hydrogen Dioxide, Hydrogen Peroxide.**—Besides water, hydrogen and oxygen form a second compound with each other. This is hydrogen peroxide. It is prepared by treating barium peroxide with sulphuric acid. The reaction that takes place will be explained under barium dioxide (which see). It is also formed by dissolving sodium peroxide (which see) in a dilute acid.

Hydrogen peroxide is a liquid that breaks up readily into water and oxygen. The ease with which it gives up oxygen makes it a good oxidizing agent. It is now manufactured on the large scale, and is used to bleach animal and vegetable substances, such as human hair, silk, wool, bone, and ivory. It is also used in restoring the color of oil paintings that have become dark with age, and works very well if the paint contains lead. It is a good antiseptic and disinfectant, and finds application in surgery on this account, and as a preservative for milk, beer, wine, and other fermentable liquids.

Analysis has shown that hydrogen peroxide contains relatively twice as much oxygen as water does. While, in the latter substance, hydrogen and oxygen are combined in the proportion of one part by weight of hydrogen to eight parts by weight of oxygen, in hydrogen peroxide there are sixteen parts by weight of oxygen to one part by weight of hydrogen.

**Summary.**—We have thus learned that (1) water can be decomposed into hydrogen and oxygen by means of an electric current; (2) the gases are obtained in the proportion of eight parts by weight of oxygen to one part by weight of hydrogen, or one volume of oxygen to two volumes of hydrogen; (3) when hydrogen is burned water is formed; (4) when hydrogen and oxygen are mixed together they do not combine under ordinary circumstances; (5) when a spark or flame is brought in contact with the mixture violent action takes place accompanied by explosion; (6) the action is occasioned by the chemical combination of the two gases; (7) they combine in the same proportions as

those in which they are obtained from water by the action of the electric current; (8) water can be made by passing hydrogen over heated copper oxide; (9) by weighing the copper oxide before and after the experiment, and determining the weight of the water formed, oxygen is found to form eight ninths of water.

**Comparison of Hydrogen and Oxygen.**—Hydrogen and oxygen are different forms of matter, just as heat and motion are different forms of energy. Heat can be converted into motion, and motion into heat, but one element cannot by any means known to us be converted into another. They are apparently entirely independent of each other. The question will therefore suggest itself, whether, in spite of their apparent independence, there is not some relation between the different elements which reveals itself by similarity in properties. It will be found that the elements can be separated into groups or families according to their properties. There are some elements, for example, which in their chemical conduct resemble oxygen markedly. These elements make up the *oxygen family*. So far as hydrogen is concerned, however, it stands by itself. There is no other element that conducts itself like it. If we compare it with oxygen, we find very few facts that indicate any analogy between the two elements. In their physical properties they are, to be sure, similar. Both are transparent, colorless, inodorous gases. On the other hand, oxygen combines readily with a large number of substances with which hydrogen does not combine. Oxygen, as we have seen, combines easily with carbon, sulphur, phosphorus, and iron. It is a difficult matter to get any of these ele-

ments to combine directly with hydrogen. Further, substances that combine readily with hydrogen do not combine readily with oxygen. The two elements exhibit opposite chemical properties. What one can do the other cannot do. This oppositeness of properties is favorable to combination; for not only do hydrogen and oxygen, with their opposite properties, combine with great ease under the proper conditions, but, as we shall see later, it is a rule that elements of like properties do not readily combine with one another, while elements of unlike properties do readily combine with one another.



## CHAPTER V.

### LAWS OF CHEMICAL COMBINATION.—COMBINING WEIGHTS. —ATOMIC WEIGHTS.—CHEMICAL EQUATIONS.

**Law of the Indestructibility of Matter.**—The work of Lavoisier in the last part of the last century showed that whenever matter is apparently destroyed it continues to exist in some other form. If it were possible to annihilate matter or to call it into being at will, it would be of little or no scientific value to weigh things. Innumerable experiments performed since Lavoisier's time have confirmed the view that *matter is indestructible*. The first fundamental law bearing upon the changes in composition which the different forms of matter undergo is the *law of the indestructibility of matter*, or the *law of the conservation of mass*. While it is perhaps impossible to conceive that this great law should not be true, it must not be forgotten that the only way by which its truth could be established was by experiment. The law may be stated thus:

*Whenever a change in the composition of a substance takes place the amount of matter after the change is the same as before the change.*

Assuming that this law has always held good, it follows that the amount of matter in the universe is the same to-day as it has been from the beginning. Transformations

are constantly taking place, but these involve no increase nor decrease in the total amount of matter.

**Law of the Conservation of Energy.**—Just as matter is neither created nor destroyed, so it has been shown that the total amount of energy is not changed. One of the greatest discoveries in science is that one form of energy can be transformed into others, and that in these transformations nothing is lost. It is now known that for a certain amount of heat a certain amount of motion can be obtained, and that for a certain amount of motion a certain amount of heat can be obtained. It is known that a similar definite relation exists between heat and electrical energy. It is known that a definite amount of heat is obtained by burning a definite amount of a given substance, and it is known also that a definite amount of heat can cause a definite amount of chemical change. Investigation has shown that all the different forms of energy are convertible one into the other without loss. This great fact is known as the *law of the conservation of energy*. Transformations of energy are constantly taking place, as transformations of matter are, but the total amount in each case remains the same.

**Law of Definite Proportions.**—Under oxygen the fact was mentioned that magnesium and oxygen combine with each other in definite proportions. This raises the question as to the proportion by weight in which other elements combine with one another. A magnet of a certain strength can support a piece of iron of a certain weight. But it will also support any piece of iron weighing less. It shows no preference for certain weights of iron. So, also, the

earth attracts all bodies, light or heavy, showing no preference for certain weights. When substances act upon one another chemically, however, it is found that a certain weight of one will combine with a definite weight of another, and only with this weight—no more and no less. Take, for example, the case of iron and sulphur. If equal weights of these elements are mixed and caused to act chemically by the aid of heat, it will be found that some of the sulphur is left in the uncombined state after the action is over. If twice as much iron as sulphur is taken, then, after the action, some iron is left. A large number of experiments have shown that when the two elements are mixed in the proportion of 7 parts by weight of iron to 4 parts of sulphur the action is perfect, neither iron nor sulphur being left.

An extensive examination has shown conclusively that any given chemical compound always contains the same elements in exactly the same proportions. The compound of sulphur and iron always contains exactly 36.36 per cent of sulphur and 63.64 per cent of iron. The compound of magnesium and oxygen always contains exactly 60 per cent of magnesium and 40 per cent of oxygen, and so on throughout the list of chemical elements. These facts were discovered by the united efforts of a large number of chemists continued through many years. They are of very great importance. They are summed up in the general statement:

*Chemical combination always takes place between definite weights of substances.*

This is known as the *law of definite proportions*. It is simply a statement of what has been found to be true in all cases studied. It must be borne in mind that this law, as well as other laws governing natural phenomena, can



never be proved to be absolutely true, for the reason that we cannot examine every case to which the law applies. But if, after examining a very large number of cases, we find that the law always holds true, we are justified in concluding that it is true of all cases. When we say that all bodies attract one another, do we know this to be absolutely true? Certainly not. But we do know that, so far as those bodies are concerned which come under our observation, the statement is true, and we therefore have every reason to believe that it is true of all bodies.

**Law of Multiple Proportions.**—It does not require a very extended study of chemical phenomena to show that from the same elements it is possible in many cases to get more than one product. Thus, iron and sulphur form three distinct compounds with each other. Tin combines with oxygen in two proportions. The elements potassium, chlorine, and oxygen combine in four different proportions, forming four distinct products. Nitrogen and oxygen form five products. In the early part of the last century the English chemist Dalton by a study of cases like those mentioned was led to the discovery of another great law of chemistry, known as the *law of multiple proportions*. Many substances had been analyzed before his time, and the percentage of the constituents determined with a fair degree of accuracy. He examined first two gases, both of which consist of carbon and hydrogen. He determined the percentages of their constituents, and found them to be as follows:

Olefiant gas, 85.7% carbon and 14.3% hydrogen;  
Marsh-gas, 75.0% carbon and 25.0% hydrogen.

On comparing these numbers he found that the ratio of carbon to hydrogen in olefiant gas is as 6:1; whereas in marsh-gas it is as 3:1 or 6:2. The weight of hydrogen, combined with a given weight of carbon, is twice as great in the one case as in the other.

There are, further, two compounds of carbon and oxygen, and in analyzing these the following figures were obtained:

Carbon monoxide, 42.86% carbon and 57.14% oxygen;

Carbon dioxide, 27.27% carbon and 72.73% oxygen.

But 42.86:57.14::3:4, and 27.27:72.73::3:8.

The weight of oxygen combined with a given weight of carbon in carbon dioxide is exactly twice as great as the weight of oxygen combined with the same weight of carbon in carbon monoxide. These facts and other similar ones led to the discovery of the law of multiple proportions, which may be stated thus:

*If two elements form several compounds with each other, the weights of one that combine with a fixed weight of the other bear a simple ratio to one another*

By simple ratio is meant that which 1 bears to 2 or to 3 or to 4, or 2 to 3, or 3 to 5.

The three compounds of iron and sulphur may serve as further illustrations. In one of them, 7 parts by weight of iron are in combination with 4 parts of sulphur; in a second, 7 parts of iron are in combination with 6 parts of sulphur; and in the third, 7 of iron are in combination with 8 of sulphur. The figures 4, 6, and 8 plainly bear a simple relation to one another. The five compounds of the element nitrogen with oxygen contain 7 parts by weight of nitrogen and 4, 8, 12, 16, and 20 parts by weight of oxygen

respectively, which figures plainly bear a simple relation to one another, viz., 1:2:3:4:5.

The law of multiple proportions, like the law of definite proportions, is simply a statement in accordance with what has been found true by experiment. Although discovered by Dalton at the beginning of the last century and put forward upon what appears now to be a slight basis of facts, all work since that time has confirmed it, and it forms to-day one of the corner-stones of the science of chemistry.

**Combining Weights of the Elements.**—A careful study of the figures representing the composition of chemical compounds reveals a remarkable fact regarding the relative quantities of one and the same element that enter into combination with different elements. The proportions by weight in which some of the elements combine chemically with one another are given in the following table:

1 part Hydrogen combines with	35.4 parts Chlorine.
1 " " " "	80 " Bromine.
1 " " " "	127 " Iodine.
35.4 parts Chlorine combine with	39 " Potassium.
80 " Bromine " "	39 " "
127 " Iodine " "	39 " "
16 " Oxygen " "	65 " Zinc.
16 " " " "	24 " Magnesium.
16 " " " "	40 " Calcium.
16 " " " "	137 " Barium.
65 " Zinc " "	32 " Sulphur.
24 " Magnesium " "	32 " "
40 " Calcium " "	32 " "
137 " Barium " "	32 " "

It will be seen that the figures that express the relative weights of chlorine, bromine, and iodine that combine with 1 part of hydrogen also express the relative weights of these

elements that combine with 39 parts of potassium. So also the figures that express the relative weights of zinc, magnesium, calcium, and barium that combine with 16 parts of oxygen express the relative weights of these elements that combine with 32 parts of sulphur. Now an examination of all compounds has shown that hydrogen enters into combination with other elements in smaller proportions than any other element does; and this element is therefore taken as unity in stating the relative weights of the other elements that enter into combination. That weight of another element that combines with 1 part by weight of hydrogen may be called its *combining weight*. Thus, according to this, the combining weights of chlorine, bromine, and iodine are respectively 35.4, 80, and 127. Similarly, 39 is the combining weight of potassium, as it expresses the weight of potassium that combines with the above weights of chlorine, bromine, and iodine. For every element a number can be selected such that the proportions by weight in which the element enters into combination with others can be conveniently expressed by this number or by a simple multiple of it. These numbers are called the combining weights.

**Hypothesis and Theory.**—The laws presented in this chapter are condensed statements that sum up what has been found true in all cases examined. They are statements of facts discovered by experiment.

When we have established a law by means of experiments, the next thing in order is to *imagine a cause*. We try to imagine a condition of things which, if it existed, would lead to the results discovered. If we succeed in imagining such a condition of things we have framed an

*hypothesis*. If, now, we test this hypothesis in every way that suggests itself, and find that all facts discovered are in accordance with it, we then call it a *theory*. An hypothesis is a guess in regard to the cause of certain phenomena. A theory is an hypothesis that has been thoroughly tested, and is applicable to a large number of related phenomena.

Hypotheses and theories are of great value to science, if founded upon a thorough knowledge of the facts to which they relate. They become dangerous when used by those who are not familiar with the facts. Those whose minds have not been properly trained are apt to be given to unprofitable speculation. The student who has not received a thorough scientific training should remember that theories and hypotheses, to be of value, must be suggested, not by a superficial but by a thorough knowledge of facts.

With these words of warning and of explanation in regard to the relation existing between the *fact*, the *law*, the *hypothesis*, and the *theory*, we may proceed to consider briefly a theory concerning the constitution of matter which grew out of the discovery of the laws of definite and multiple proportions.

**The Atomic Theory.**—If we consider any simple form of matter or element, such as iron, it is clear that there are two views that may be held regarding the way the substance is made up. We know that we can subdivide every piece of iron we can see, no matter how small it may be; and though after a time the particles would become so small that we could no longer subdivide them, still we can imagine that by more refined methods the process of subdivision might be continued without end. If we believe that such

infinite subdivision is possible, we hold the hypothesis that matter is infinitely divisible. We cannot prove this—we can only speculate in regard to it. But we may also conceive that after the process of subdivision has been carried on for a time, until very minute particles have been obtained, a limit can be reached beyond which the process of subdivision cannot be carried. If we believe this, we hold the hypothesis that matter is not infinitely divisible, or that matter consists of *indivisible particles*. These particles may be called *atoms* (from the Greek *ἄτομος*, which signifies indivisible). Both of these hypotheses have been held for ages. But the discussion in regard to the relative merits of the two views was at first not much more profitable than it would be if carried on between two students who are in the early stages of their study of the facts.

When the laws of definite and multiple proportions were discovered by Dalton, he saw that the conception that matter is made up of indivisible particles or atoms might have some connection with the laws. If each element is made up of atoms, the most probable view is that every atom of any particular element is exactly like every other atom of that element. Among the properties possessed by these atoms must be weight. It is probable that the atoms of different elements have different weights. Suppose now that, when chemical combination takes place between two elements, the action takes place between these atoms, so that one atom of the one element combines with one of the other, and so on through the mass. If there were present in one mass exactly as many atoms as in the other, both elements would enter completely into combination—nothing would be left over. But if there were a

larger number of atoms of one element than of the other, then, of the element of which the larger number of atoms is present, some would be left over after the action is complete. Suppose, further, that the weights of the atoms of two elements are to each other as 1:10. Then, if, when these two elements are brought together, they combine in the proportion of one atom of one to one atom of the other, the resulting compound will contain the elements in the proportion of 1 part by weight of one to 10 parts by weight of the other. Or if, on analyzing a compound of two elements, we find that it contains 1 part by weight of one to 10 parts by weight of the other, we conclude that the weights of the atoms of the two elements bear to each other the relation 1:10.

If matter consists of atoms, and chemical action takes place between these atoms, we can understand why chemical action takes place between definite weights of substances; in other words, we see a probable reason for the law of definite proportions. As the atoms are supposed to be indivisible, if two elements combine in more than one proportion with each other, they must do so in the proportion of one atom of one to two atoms of the other, or one to three, or two to three, or in some other way that does not involve the breaking-up of the atoms. If, for example, two elements, the weights of whose atoms are as 1 to 10, combine in the proportion of one atom of one to one atom of the other, the resulting compound will contain the elements in the proportion of 1 part by weight of one to 10 parts by weight of the other element. If the same elements combine in the proportion of one atom of the first to two atoms of the other, then the resulting com-

pound will contain the elements in the proportion of 1 part by weight of one to 20 parts by weight of the other, and so on. It will thus be seen that if two elements combine in more than one proportion with each other, and the view that matter consists of atoms of definite weight, and that chemical action takes place between these atoms, is correct, then it follows that the elements must combine in accordance with the law of multiple proportions.

**Atomic Weights.**—A thorough study of the facts has shown that the atomic theory, as suggested by Dalton, is the simplest conception that can be formed in regard to the constitution of matter which will satisfactorily account for the laws of definite and multiple proportions. The weights of the elements which have thus far been referred to as *combining weights* are, in accordance with the theory, the relative weights of the atoms, or the *atomic weights*. The symbols of the elements represent atoms of the elements. Thus H represents an atom of hydrogen, O an atom of oxygen, Cl an atom of chlorine, etc. The combining weights, found by analyzing compounds in which these elements occur, are  $H=1$ ,  $O=16$ , and  $Cl=35.4$ . That is to say, by means of these figures we can always represent the relative weights of the elements found in their compounds. Hydrochloric acid, for example, contains hydrogen and chlorine in the proportion of 1 part hydrogen to 35.4 parts chlorine. Hence it is believed that the weight of the atom of hydrogen is to that of chlorine as 1 to 35.4. As hydrogen enters into combination in smaller proportion than any other element, its combining weight or atomic weight is taken as the unit, and all others compared with it.



If we say that the atomic weight of oxygen is 16, and that of chlorine is 35.4, we mean simply that the atom of oxygen is 16 times heavier and that of chlorine 35.4 times heavier than that of hydrogen. We might take any other standard, but that of the hydrogen atom is the simplest. At one time the atomic weight of oxygen was taken as 100, and then the atomic weights of the other elements were correspondingly larger.

[PROBLEM.—If we call the atomic weight of oxygen 100, what would those of hydrogen and chlorine be? The atomic weight of hydrogen being accepted as 1, those of oxygen and chlorine are 16 and 35.4 respectively.]

#### **How the Relative Weights of the Atoms are Determined.**

—If we could isolate atoms and weigh them, there would be no serious difficulty in determining their relative weights. But as we cannot deal with atoms, we must deal with collections of atoms, and from a study of these collections draw conclusions regarding the weights of the atoms themselves.

If it were the rule that two elements combine with each other in only one proportion, it might be safe to conclude that they combine in the proportion of one atom of one to one atom of the other. Then, by simply determining the weights of the elements contained in a definite weight of the compound, we should be in a position to draw conclusions regarding the relative weights of the atoms. But suppose two elements combine in more than one proportion. For example, nitrogen and oxygen combine in these proportions: 14 of nitrogen to 8 of oxygen, 7 of nitrogen to 8 of oxygen, 7 of nitrogen to 16 of oxygen, and it is required from these figures to determine the relative weights of the

atoms of nitrogen and oxygen. We may suppose that in the first compound the elements are combined atom to atom, then the relative weights of these atoms are 14 for nitrogen to 8 for oxygen. If, however, we had already concluded from a study of the compounds of hydrogen and oxygen that the atom of oxygen is 16 times heavier than that of hydrogen, we should have in the above compound of nitrogen and oxygen 28 parts of nitrogen combined with 16 parts of oxygen, and the atomic weight of nitrogen would appear to be 28. But we may equally well assume that in this compound 2 atoms of nitrogen are combined with 1 atom of oxygen. This idea would be represented by the formula  $N_2O$ , and, if we accept this conception, the atomic weight of nitrogen must be 14. This example will suffice to show that the determination of the relative weights of atoms by means of the analysis of compounds is a difficult matter, and that attempts to make the determinations in this way would necessarily lead us into difficulties which we could not surmount without the aid of some new conception to aid us to determine the number of atoms contained in the smallest particles of compounds. The difficulties have been largely overcome, as will be shown farther on, and the atomic weights accepted at the present day have been determined by the aid of a number of methods

**Formulas of Chemical Compounds.—Molecules.**—Chemical compounds are represented by placing the symbols of the constituent elements side by side. Thus  $HCl$  means a compound of hydrogen and chlorine in which these elements are present in the proportion of 1 part by weight of hydrogen to 35.4 parts by weight of chlorine, or in terms

of the atomic theory it means a compound whose smallest particle is made up of an atom of hydrogen and an atom of chlorine. The formula  $\text{H}_2\text{O}$  stands for a compound whose smallest particle is made up of two atoms of hydrogen and one of oxygen; and  $\text{H}_2\text{O}_2$  stands for a compound whose smallest particle consists of two atoms of hydrogen and two atoms of oxygen. The small figure placed to the right below the symbol of an element shows the number of atoms of the element in the smallest particle of the compound, and, of course,—and this is of chief importance at this stage,—it shows the proportion by weight in which the element is contained in the compound. These smallest particles of compounds are called *molecules*. The relation between these and atoms, and the methods of determining molecular weights, will be discussed farther on. The formula  $\text{HCl}$  represents, then, a *molecule* of hydrochloric acid made up of one atom of hydrogen and one atom of chlorine;  $\text{H}_2\text{O}$  represents a *molecule* of water;  $\text{HgO}$ , a *molecule* of mercuric oxide;  $\text{MnO}_2$ , a *molecule* of manganese dioxide;  $\text{KClO}_3$ , a *molecule* of potassium chlorate;  $\text{ZnSO}_4$ , a *molecule* of zinc sulphate. These formulas are of great convenience in representing chemical reactions.

**Summary.**—All experience shows that matter is indestructible, that energy is indestructible, and that chemical combination takes place according to the laws of definite and multiple proportions.

For each element a number can be selected by means of which the proportions by weight in which the element enters into combination with others can be conveniently expressed. Such a number is called the combining weight.

An hypothesis is a guess as to the cause of certain phenomena.

A theory is an hypothesis that has been thoroughly tested, and is applicable to a large number of related phenomena.

According to the atomic theory every element is made up of particles, called atoms, that are indivisible in chemical reactions. The atom of every element has a characteristic, definite weight.

Methods have been devised for determining the relative weights of the atoms.

A molecule\* is made up of atoms, and is the smallest particle of a compound.

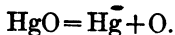
\*The expression molecule of an element will be explained farther on (see page 196).

## CHAPTER VI.

### STUDY OF THE REACTIONS EMPLOYED IN THE PREPARATION OF OXYGEN AND OF HYDROGEN AND IN THE STUDY OF WATER.

**Preparation of Oxygen.**—The reactions employed in the preparation of oxygen were: (1) The decomposition of mercuric oxide by heat; (2) The decomposition of potassium chlorate by heat; (3) The decomposition of manganese dioxide by heat; (4) The action of heat on a mixture of potassium chlorate and manganese dioxide; (5) The action of water on oxone and (6) The action of heat on barium oxide.

**Heating Mercuric Oxide.**—When mercuric oxide is heated it is decomposed, yielding mercury and oxygen. This was shown in Exp. 3. But analysis shows that mercuric oxide consists of mercury and oxygen combined in the proportion of their atomic weights, 200 parts of mercury to 16 parts of oxygen; and it has been shown that when decomposition takes place, mercury and oxygen are obtained in these proportions. These facts are represented by the simple equation



This equation expresses the reaction *qualitatively* and *quantitatively*; and it must be remembered that it differs from algebraic equations in this important respect, that it

expresses something that has been established by experiment. *Chemical equations cannot be solved by mental processes alone, as algebraic equations can.*

**Quantitative Study of the Decomposition of Potassium Chlorate by Heat.**—Potassium chlorate is made up as represented by the formula  $\text{KClO}_3$ , or its molecule consists of an atom of potassium, an atom of chlorine, and three atoms of oxygen. The atomic weights of these elements are respectively  $\text{K}=39$ ;  $\text{Cl}=35.4$ ; and  $\text{O}=16$ . That is to say, the compound consists of these elements in the proportion of 39 parts of potassium; 35.4 parts of chlorine; and  $48(3 \times 16)$  parts of oxygen.

It is, therefore, an easy matter to calculate how much oxygen, or chlorine, or potassium any given weight of potassium chlorate contains. Let it be required, for example, to calculate how much oxygen is contained in 4 grams of potassium chlorate. As the compound is made up of 39 parts of potassium, combined with 35.4 parts of chlorine and 48 parts of oxygen, in  $39+35.4+48=122.4$  parts of potassium chlorate there are 48 parts of oxygen. If in 122.4 parts there are 48 parts, how much is there in 4 grams? Plainly the answer is given by the solution of the simple proportion

$$122.4:48::4:x,$$

in which  $x$  represents the actual weight of oxygen contained in 4 grams of potassium chlorate. Similarly the proportion

$$122.4:39::4:x$$

will give the weight of potassium, and

$$122.4:35.4::4:x$$

will give the weight of chlorine contained in 4 grams of potassium chlorate.

When potassium chlorate is heated until no more oxygen is given off, the compound potassium chloride, of the formula  $\text{KCl}$ , is left behind. By weighing the potassium chlorate taken and the potassium chloride left, and measuring the oxygen given off, it has been shown that the relative weights of the substances are represented by the equation

$$\begin{array}{rcccl} \text{KClO}_3 & = & \text{KCl} & + & 3\text{O} \\ \hline 39 + 35.4 + 48 & & 39 + 35.4 & & 3 \times 16 \\ \hline 122.4 & & 74.4 & & 48 \end{array}$$

That is to say, 122.4 grams of potassium chlorate gives 74.4 grams of potassium chloride and 48 grams of oxygen. The figure 3 before the symbol of oxygen means three atoms of oxygen. When the element is in combination, the figure expressing the number of atoms is placed to the right of the symbol, below the line, as in the formula of potassium chlorate.

#### THE WEIGHT OF OXYGEN IN A GIVEN WEIGHT OF POTASSIUM CHLORATE.

*Experiment 50.*—To determine how much oxygen is given off when a known weight of potassium chlorate is decomposed by heat, proceed as follows: In a small dry hard-glass tube about 10 cm. (4 in.) long and 8 to 10 mm. (about  $\frac{1}{4}$  in.) internal diameter, closed at one end, weigh out on a chemical balance about 0.2 gram dry potassium chlorate, first weighing the tube empty. Introduce just above the potassium chlorate a plug of asbestos, then soften the tube in a flame, and draw it out so that it has the form shown in Fig. 23, the plug of asbestos being at the constricted part *B* of the tube. Now weigh the tube again.

Let  $a$  = weight of tube empty;

$b$  = weight of tube with potassium chlorate;

$c$  = weight of tube with potassium chlorate and plug.

Connect at  $A$  by means of a short piece of rubber tubing with a measuring-tube (see Appendix II) so that the ends of the two tubes are almost in contact with each other, the measuring-tube having been previously filled with water to the zero-point, and the top closed by means of the stop-cock. Open the stop-cock, and now heat the potassium chlorate, gently at first, and gradually higher until no more gas is given off. After the gas has stood for half an hour to cool it down to the temperature of the air, adjust the two tubes of the measuring-apparatus so that the level of the

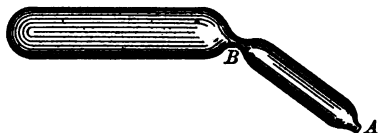


FIG. 23.

water in both is the same; read off the volume of the gas. At the same time read the barometer and thermometer; and now make the corrections for pressure and temperature as directed in Appendix II. The weight of a litre or 1000 cc. of oxygen at 0 and 760 mm. pressure is 1.429 grams. Knowing the volume of oxygen obtained, calculate the weight of this volume. Remove the tube containing the product left after the decomposition of the potassium chlorate and weigh it.

Let  $d$  = weight of tube after decomposition of potassium chlorate. Then

$b - a$  = weight of potassium chlorate used,

$c - d$  = loss in weight = oxygen.

This should, of course, be the same as the weight of oxygen found by measuring that given off and calculating the weight from the volume.

Further,

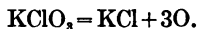
$c - b$  = weight of plug;



and  $d = \text{weight of tube} + \text{weight of plug} + \text{weight of potassium chloride};$

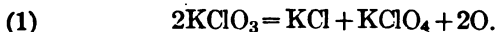
and  $d - (a + c - b) = \text{weight of potassium chloride}.$

Make all the calculations, and see how nearly the results obtained agree with the equation



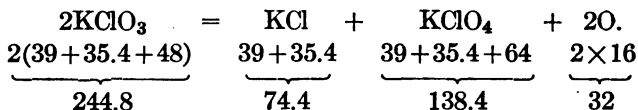
Should the results not be satisfactory the first time, repeat the work. The more carefully the work is done the more nearly will the results agree with the equation.

In Exp. 17 (p. 26) a fact was observed which is not taken account of in the equation  $\text{KClO}_3 = \text{KCl} + 3\text{O}$ . It was seen that the gas was given off in two stages: first, a part came off at a comparatively low temperature, and then a larger quantity came off at a higher temperature. If the gas given off during the first stage had been measured, it would have been found to be only one third of the total obtained by complete decomposition. If, further, the solid substance left behind in the flask had been properly examined, it would have been found to consist of two substances, one of which was potassium chloride,  $\text{KCl}$ , and the other a compound that contains more oxygen than the chlorate. The latter is potassium perchlorate,  $\text{KClO}_4$ . The relative quantities of the two substances would also have been found to correspond to the weights represented by the formulas  $\text{KCl}$  and  $\text{KClO}_4$ , i.e., there would have been found  $39 + 35.4 = 74.4$  parts of potassium chloride to  $39 + 35.4 + 4 \times 16 = 138.4$  parts of potassium perchlorate. The following equation expresses these facts:



U. of M.

The figure 2 placed before the formula of potassium chlorate affects the whole formula, so that the quantitative relations are represented thus:



In the second stage of the decomposition all the rest of the oxygen is given off, or, in other words, the potassium perchlorate is now decomposed, thus:



The complete change is represented by the equation



[PROBLEMS.—How much potassium chlorate must be taken to get 10 litres of oxygen? (Equation (3) shows the proportions of the substances involved.) In this case how much potassium perchlorate and how much potassium chloride would be formed? How much potassium chloride would 5 grams of potassium chlorate yield? How much potassium perchlorate? (Equation (1) shows these relations.) What volume of oxygen would be obtained by heating 20 grams of potassium chlorate until the first stage of the decomposition is complete?]

**Heating Manganese Dioxide.**—The change effected in manganese dioxide by heat is represented by the equation

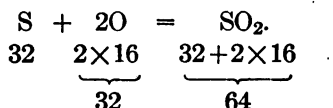


The atomic weight of manganese being 55, the quantitative relations may be readily calculated.

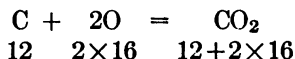
[PROBLEMS.—How much oxygen can be obtained by heating 12 grams of manganese dioxide? How much manganese dioxide must be heated in order to get 3 grams of oxygen? In each case how much of the compound  $\text{Mn}_3\text{O}_4$  would be obtained?]

**The Action of Oxygen on Carbon, Sulphur, Phosphorus, and Iron.**—The general character of the action of oxygen on the elements named has been discussed in connection with Experiments 21, 22, 23, and 24 (see page 31), and evidence was presented to show that the action consists in direct union which results in the formation of new compounds called oxides. But the quantitative relations were not referred to. These relations must, of course, be determined by experiment. The substance burned, the oxygen used up, and the product formed must in each case be weighed. This has been done repeatedly, and it will suffice here to give the results.

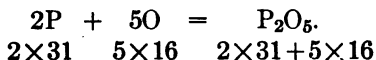
When sulphur burns in oxygen, for every 32 parts of sulphur burned 32 parts of oxygen are used up, and 64 parts of sulphur dioxide,  $\text{SO}_2$ , are formed:



In the case of carbon it has been shown that for every 12 parts of carbon burned 32 parts of oxygen disappear, and there are formed 44 parts of the compound carbon dioxide,  $\text{CO}_2$ . The equation representing the action is

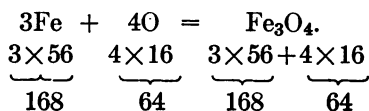


In the case of phosphorus, for every 62 parts of this element that disappear, 80 parts of oxygen are used up, and 142 parts of the compound  $\text{P}_2\text{O}_5$  are formed, as represented in the equation

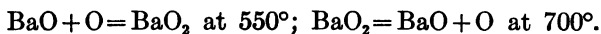


The compound  $P_2O_5$  is known as phosphorus pentoxide. It is the white substance found in the vessel.

When iron burns in oxygen the product formed is magnetic oxide of iron,  $Fe_3O_4$ :

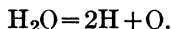


The reaction in Brins process for obtaining oxygen from barium dioxide are:



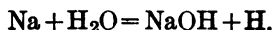
**Preparation of Hydrogen.**—The reactions by which hydrogen can be most readily prepared are: (1) The decomposition of water by an electric current; (2) The action of sodium and of potassium on water; (3) The action of iron on water; (4) The action of carbon on water; (5) The action of metals on acids.

**Decomposition of Water by an Electric Current.**—This reaction has been studied somewhat fully in connection with the subject of water. The facts established show that it is represented by the equation

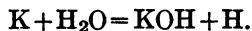


**Action of Sodium and Potassium on Water.**—**Substitution.**—The fact that when sodium is thrown on water hydrogen is given off was shown in Exp. 27 (see page 45). Attention was also called to the fact that there is something in the water after the action is over. Analysis of this substance has shown that it has the composition represented

by the formula  $\text{NaOH}$ . It is called caustic soda or sodium hydroxide. The reaction between sodium and water is represented by the equation

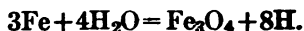


According to this, each molecule of water gives up one atom of hydrogen and an atom of sodium takes its place. The sodium is substituted for hydrogen in the water. This action is plainly different in kind from any that has thus far been studied. Those are either simple acts of combination, as the action of oxygen on sulphur, or of decomposition, as the action of heat on mercuric oxide and on potassium chlorate. The action of sodium on water, however, is an act of *substitution*, which involves both combination and decomposition. The water is decomposed and the sodium hydroxide is formed by combination. Potassium acts upon water in the same way as sodium, and the reaction is represented thus:



Potassium acts on water more rapidly than sodium does, so that the amount of heat evolved in a given time is greater than in the case of sodium, and the temperature is therefore raised high enough to set fire to the hydrogen. If the motion of the sodium is interfered with by putting the metal on a piece of filter-paper laid upon the water, the temperature becomes high enough to set fire to the gas, as in the case of potassium. This restriction of the motion of the sodium simply prevents it from being cooled off, as it is when it moves over the surface of the water.

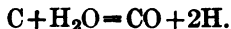
**Action of Iron on Water.**—At ordinary temperatures iron does not readily act on water, but when steam is passed over heated iron, as in Exp. 28 (see page 47), action takes place according to this equation:



For another method of formation of the compound  $\text{Fe}_3\text{O}_4$  see Exp. 24, page 31, and also page 38.

[**PROBLEMS.**—The atomic weight of iron is 56; how much water can be decomposed by 20 kilograms (or 40 pounds) of iron? and how much would the hydrogen obtained weigh? One litre of hydrogen at  $0^\circ \text{C}$ . and under the standard pressure of 760 mm. weighs 0.08995 gram; what will be the volume of hydrogen obtained by using up 20 kilograms of iron in the decomposition of water?]

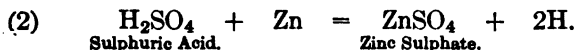
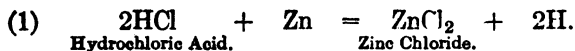
**Decomposition of Water by Carbon.**—This decomposition gives the mixture known as “water-gas.” The action is represented by the equation



The gas CO is carbon monoxide, which will be studied later.

[**PROBLEM.**—The reaction represented by the last equation yields equal volumes of carbon monoxide and of hydrogen. How much water would 5 kilograms (or 10 pounds) of carbon (atom. wt. = 12) decompose, and what volume of gas would be obtained?]

**Action of Metals on Acids.**—The action of zinc on hydrochloric acid and on sulphuric acid was studied in Exp. 29 (see pages 49, 51), and it was stated that in each case the zinc takes the place of the hydrogen in the acid. The two reactions are thus represented:



In Exp. 36 (see page 56) the zinc sulphate formed was obtained in the form of crystals. It will be seen that the action of zinc on hydrochloric acid and on sulphuric acid is of the same kind as the action of sodium and of potassium on water. It is *substitution*. The zinc takes the place of the hydrogen. Another point of interest to be noted is that while an atom of sodium takes the place of one atom of hydrogen, an atom of zinc takes the place of two atoms of hydrogen. It will be seen later that there are elements whose atoms have the power of taking the place of three atoms of hydrogen, and others with still higher substituting values.

**Quantitative Study of the Action of Acids on Metals.—**  
One example, that of sulphuric acid, will suffice.

#### ACTION OF SULPHURIC ACID ON ZINC.

*Experiment 51.*—The amount of hydrogen evolved when a known weight of zinc is dissolved in sulphuric acid can be determined by means of the apparatus represented in Fig. 24. The bent tube leading from the flask *A* is drawn out at *B*, and a plug of glass-wool introduced below the constriction. The other parts of the apparatus need no description. The flask should have a capacity of about 40 to 50 cc.; and the measuring-tube *C* should have a capacity of about 100 cc., and be graduated in  $\frac{1}{16}$  cc. Fill *D* with distilled water that has been boiled; put a piece of zinc weighing from 0.15 to 0.20 gram in the flask; open the pinch-cock *E*, by which means the whole apparatus is filled with water. Examine the apparatus to see whether gas-bubbles are lodged

under the stopper *F* or in the glass-wool. If so, they can usually be dislodged without difficulty. If they persist, boil the water for a few moments. Now place the measuring-tube *C* in position and let the greater part of the water remaining in *D* flow through the apparatus. Into this tube *D* then pour dilute sulphuric acid (1 of

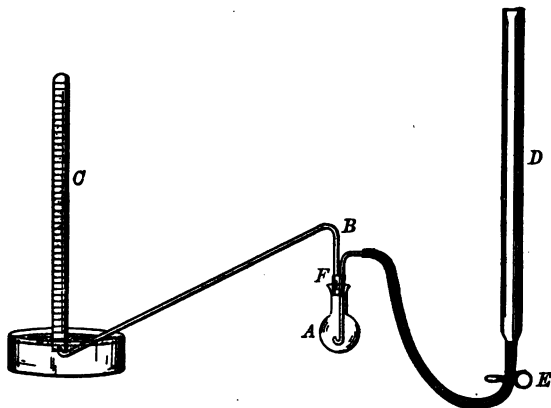


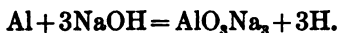
FIG. 24.

acid to 4 of water) until it is nearly full. Open the pinch-cock *E*, and thus displace the water which fills the apparatus. The action of acid upon the metal is facilitated by heat or by adding with the zinc a few small pieces of platinum. When the action is over, sweep the contents of the flask through the delivery-tube by again opening the pinch-cock *E*. Finally, the measuring-tube is transferred to a cylinder of water, and the volume of the gas read and corrected in the usual manner.\* How much does the hydrogen obtained in the experiment weigh? How much ought to have been obtained? How many cubic centimetres ought to have been obtained?

\* For the laws of gases and methods of measuring gas volumes see Appendix II.

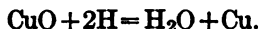


Hydrogen is prepared technically by the electrolysis of sodium hydroxide solution, and by decomposing dilute sodium hydroxide by aluminium. The first of these reactions is explained on page 54. The second is



the products being sodium aluminate which remains in solution and hydrogen.

**Action of Hydrogen on Copper Oxide**—In Exp. 46, page 64, it was shown that when hydrogen is passed over heated copper oxide, water is formed and copper is left in the tube. The action is represented by the equation

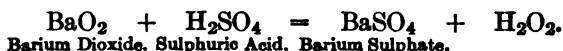


Here, it will be observed, two atoms of hydrogen take the place of one atom of copper in the oxide. (Compare the action of zinc on sulphuric acid with that of hydrogen on copper oxide.)

[**PROBLEM.**—The atomic weight of copper is 63.6; how much water would be formed by reducing 5 grams of copper oxide? How much hydrogen would be necessary?]

**Preparation of Hydrogen Dioxide.**—**Double Decomposition.**—Hydrogen dioxide (see page 76) consists of hydrogen and oxygen combined in the proportion of 1 part by weight of hydrogen to 16 parts by weight of oxygen. By methods that will be discussed later it will be shown that the molecule of this compound consists of two atoms of hydrogen combined with two atoms of oxygen, its formula

being  $\text{H}_2\text{O}_2$ . Its formation from barium dioxide by the action of sulphuric acid is represented thus:



In some respects this reaction differs from all others thus far studied. Here, two *compounds* acting upon each other give two new *compounds*. There is an exchange of constituents. This kind of action is called *double decomposition*, or *metathesis*. It is by far the most common kind of chemical action with which we have to deal.

**Kinds of Chemical Reaction.**—There are then four kinds of chemical reactions, and all these have been illustrated by examples. They are: (1) *Direct Combination*; (2) *Direct Decomposition*; (3) *Substitution*; and (4) *Double Decomposition*, or *Metathesis*.

**Conditions under which Chemical Reactions Take Place.**  
—Chemical reactions take place under the greatest variety of conditions. Some take place by simply bringing the substances together at ordinary temperature, as, for example, when sodium and potassium act on water. Others take place on heating the substances together, as, for example, when iron decomposes water, and hydrogen decomposes copper oxide. In most of the reactions thus far studied, and indeed in most of those which will be studied, heat is employed, as it generally aids chemical action. Some reactions take place in solution. That this is a great aid to chemical action has already been pointed out (see page 75). Some substances are so unstable that they are decomposed

by the touch of a feather, as, for example, a compound of iodine and nitrogen. Others are so stable that they resist the action of the highest temperatures. The electric current has a very marked effect upon many chemical compounds, especially if they are in solution or in molten condition. This has been illustrated by the action of the current on water, the result being, as will be remembered, the setting free of the two gases oxygen and hydrogen. Again, reactions differ very much in respect to their violence, from the most terrific explosions to the quiet action of the air in our lungs, and of carbon dioxide in the leaves of plants.

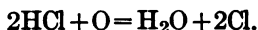
## CHAPTER VII.

### CHLORINE AND ITS COMPOUNDS WITH HYDROGEN AND OXYGEN.

**Occurrence.**—Chlorine, though widely distributed in nature, does not occur in very large quantity as compared with oxygen and hydrogen. It is found chiefly in combination with the element sodium as common salt, or sodium chloride, which has the composition represented by the formula  $\text{NaCl}$ . It is also found in combination with other elements, as potassium, magnesium, etc. In comparatively small quantity it occurs in combination with silver, forming one of the most valuable silver ores.

**Preparation.**—The simplest method of preparing chlorine, and the one that is largely used in the arts, consists in passing a strong electric current through a water solution of sodium chloride. This causes chlorine and sodium to appear at the poles of the battery. The chlorine escapes as such, while the sodium acts upon the water, forming hydrogen and sodium hydroxide or caustic soda (see Sodium Hydroxide). Chlorine is also obtained on the large scale by the action of an electric current on a solution of potassium chloride or of zinc chloride; and on some other compounds of chlorine.

In the laboratory chlorine is made by oxidizing hydrochloric acid. Under proper conditions the action represented in the following equation takes place:



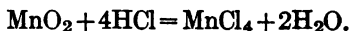
**Deacon's Process.**—As there is an unlimited supply of oxygen in the air, it would be advantageous to effect the decomposition of hydrochloric acid by means of the element in the free state. On the large scale this can be accomplished. Deacon's process for manufacturing chlorine consists in passing air and hydrochloric acid together through a heated tube containing clay balls saturated with copper sulphate. Exactly why the oxidation takes place under these circumstances is not known. The essential feature of the reaction is nevertheless the oxidation of the hydrochloric acid, as represented in the above equation.

**Laboratory Method.**—For the preparation of chlorine in the laboratory it is most convenient to bring hydrochloric acid in contact with manganese dioxide,  $\text{MnO}_2$ , a substance which has been employed for the purpose of preparing oxygen (see page 26). The action is explained thus: In the first place, when hydrochloric acid acts upon many compounds containing oxygen, the hydrogen and oxygen combine, and the element which was in combination with oxygen combines with chlorine. Thus, when the compound  $\text{MnO}$  is treated with hydrochloric acid, this reaction takes place:



So, also, when manganese dioxide is treated with hydrochloric acid, chlorine is probably first substituted for the

oxygen, as represented in the equation



But the compound  $\text{MnCl}_4$  gives up half of its chlorine when gently heated:



So that the action of hydrochloric acid on manganese dioxide is represented as follows:



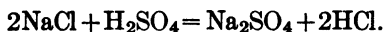
[PROBLEM.—How much manganese dioxide would be required to liberate 50 grams of chlorine? The atomic weight of manganese is 55.]

Instead of first making the hydrochloric acid from salt and then treating the hydrochloric acid with manganese dioxide, it is simpler to mix together the manganese dioxide and common salt and pour upon the mixture the necessary quantity of sulphuric acid. The reaction takes place according to the following equation:



The products formed are sodium sulphate,  $\text{Na}_2\text{SO}_4$ , manganese sulphate,  $\text{MnSO}_4$ , water,  $\text{H}_2\text{O}$ , and chlorine.

When sulphuric acid acts upon sodium chloride alone the products are sodium sulphate,  $\text{Na}_2\text{SO}_4$ , and hydrochloric acid,  $\text{HCl}$ :



The best method of obtaining chlorine for laboratory use is to treat bleaching powder with commercial hydrochloric acid in a Kipp's apparatus (see Fig. 13a, p. 51); chlorine is instantly generated under pressure enough to

force it through a drying apparatus if desired, and the current can be regulated at will.

#### ACTION OF SULPHURIC ACID ON SALT.

*Experiment 52.*—Pour 2 or 3 cc. concentrated sulphuric acid on a gram or two of common salt in a test-tube. Heat gently. Describe all that you observe. Hydrochloric acid and sodium sulphate are formed.

#### CHLORINE.

*Experiment 53.*—This experiment should be carried on under a hood. Arrange an apparatus as shown in Fig. 25. The flask need not, of course, be of the shape shown in the figure, but may be of any kind available. It should have a capacity of about 1 litre. The collecting vessel should be a clean, dry cylinder or bottle of colorless glass. The mouth of this vessel should be covered with a piece of paper to prevent currents of air from carrying away the chlorine. The delivery-tube should extend to the bottom of the collecting vessel, as the chlorine can thus readily displace the air. The chlorine is heavier than the air and therefore remains below it. By the color the experimenter can judge of the quantity of chlorine present in the vessel. A satisfactory method of making chlorine is this: Mix 5 parts by weight of coarsely granulated common salt and 5 of coarsely granulated manganese dioxide. Make a mixture of 12 parts by weight of concentrated sulphuric acid and 6 of water.\* Let this mixture cool down to the ordinary temperature, and then pour it on the

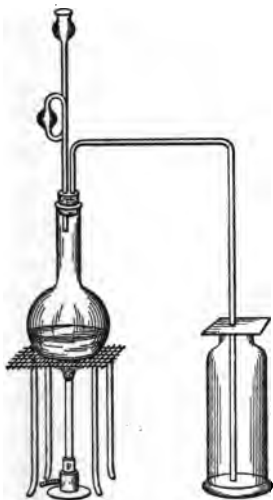


FIG. 25.

concentrated sulphuric acid and 6 of water.\* Let this mixture cool down to the ordinary temperature, and then pour it on the

\* See precautions noted on page 48.

mixture of manganese dioxide and common salt. Use 50 grams manganese dioxide and the other substances in the proportions above stated. Heat very gently and collect six or eight dry cylinders or bottles full of chlorine.

(1) Sprinkle into one of the vessels containing chlorine a little finely powdered antimony. The two elements combine at once with evolution of light. The product is antimony trichloride,  $\text{SbCl}_3$ .

[In what respects does this experiment resemble the one in which iron was burned in oxygen? In what respects do the two differ?]

(2) Into a second vessel introduce a few pieces of heated thin copper foil, or a sheet of Dutch foil. Combination takes place with evolution of light and heat.

(3) Into a third vessel introduce a piece of paper with some writing on it, some flowers, and pieces of colored calico. Most of the colors will be destroyed *if the substances are moist*.

(4) Into a fourth vessel introduce a dry piece of the same colored calico as that used in the previous experiment. What difference do you observe between the dry piece and the moist piece?

**Properties of Chlorine.**—Chlorine is a greenish-yellow gas. It has a disagreeable smell, and acts upon the passages of the throat and nose, causing irritation and inflammation. The effect is much like that of a "cold in the head." Inhaled in concentrated condition, i.e., not diluted with a great deal of air, it would cause death. It is much heavier than air, its specific gravity being 2.49. A litre of chlorine gas, under standard conditions, weighs 3.22 grams. It is soluble in water and acts upon mercury, and therefore cannot be collected by displacement of either of these liquids. The most convenient way to collect it is by upward displacement of air as in the experiment. It is easily con-



densed to the liquid form, and it can now be had in the market in this form.

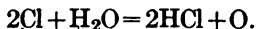
**Action of Chlorine.**—From the experiments it is seen that chlorine combines readily with other substances, and also that it destroys colors, or bleaches. It is indeed one of the most active elements. It not only acts directly upon many of the elements at ordinary temperatures, and decomposes many compounds, but it also acts upon most organic substances, or such as are formed as the products of animal or vegetable life. Its action upon the tissues of the respiratory organs has already been noticed.

#### ABSTRACTION OF HYDROGEN BY CHLORINE.

*Experiment 54.*—Perform this experiment under a hood. Cut a piece of filter-paper or tissue-paper about an inch wide and six to eight inches long. Pour on this some ordinary oil of turpentine previously warmed slightly. Introduce this into a vessel of chlorine. What takes place?

Oil of turpentine consists of carbon and hydrogen. The main action of the chlorine in this case consists in extracting the hydrogen and leaving the carbon. The experiment is interesting chiefly in so far as it illustrates the general tendency of chlorine to act upon vegetable substances.

**Bleaching by Chlorine.**—It has been noticed (see (3) and (4) page 114) that when moisture is present chlorine bleaches, while when it is not present bleaching does not take place. It has been shown that chlorine acts directly upon some dye-stuffs, converting them into colorless substances. In other cases the destruction of the color is due to oxygen, which is set free from water by the action of chlorine. In the direct sunlight chlorine decomposes water according to this equation:



In bleaching, this decomposition of water takes place in direct contact with the colored materials, and the oxygen, the instant it is set free (see paragraph on "Nascent State"), is more active than free oxygen. It is this oxygen which is being set free that acts upon the colored substance and converts them into colorless substances.

#### DECOMPOSITION OF CHLORINE-WATER.

*Experiment 55.*—(T) Seal one end of a glass tube about a metre (or about a yard) long and about 12 mm. ( $\frac{1}{2}$  inch) internal diameter. Fill this with a strong solution of chlorine in water. Invert it, as shown in Fig. 26, in a shallow vessel containing some of the same solution of chlorine in water. Place the tube in direct sunlight and leave it for a day or two. What change in color of the solution, in the odor, taste? What does the gas appear to be?

#### DIRECT UNION OF CHLORINE AND HYDROGEN.

*Experiment 56.*—Light a jet of hydrogen in the air and carefully introduce it into a vessel containing chlorine. Does it continue to burn? Is there any change in the appearance of the flame? Is there any evidence of the formation of a gas that differs from hydrogen and from chlorine? In what other experiment has this gas been met with? (see page 113).



FIG. 26.

**Hydrogen Burns in Chlorine.**—The ease with which chlorine decomposes water and vegetable substances containing hydrogen shows that it readily combines with hydrogen. Just as hydrogen burns in oxygen, it also burns in chlorine.

The burning of hydrogen in air or oxygen is simply the act of combination of hydrogen and oxygen, the product being water in the state of vapor, and therefore invisible. When hydrogen burns in chlorine the action consists in the union of the two gases, the product being hydrochloric acid,  $\text{HCl}$ , which combines with water from the air and forms clouds. In both cases the action is accompanied by an evolution of heat and light.

**Chlorides.**—Just as the compounds of oxygen with other elements are called oxides, so the compounds of chlorine with other elements are called *chlorides*.

**Nomenclature of Chlorides and of Oxides.**—The chlorides are named in the same way as the oxides. The name of the element with which the chlorine is combined is prefixed. Thus the compound of zinc and chlorine,  $\text{ZnCl}_2$ , is called zinc chloride; that of sodium and chlorine,  $\text{NaCl}$ , sodium chloride, etc. When an element forms more than one compound with oxygen, suffixes are used to distinguish them. Thus in the case of copper there are two oxides which have the formulas  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ . The former, which contains the smaller proportion of oxygen, is called *cuprous oxide*, while the latter, which contains the larger proportion of oxygen, is called *cupric oxide*. In general, of two oxides of the same element, that which contains the smaller proportion of oxygen is designated by the suffix *ous*, while that which contains the larger proportion is designated by the suffix *ic*. *Ferrous oxide* has the composition  $\text{FeO}$ ; *ferric oxide*,  $\text{Fe}_2\text{O}_3$ ; *manganous oxide* is  $\text{MnO}$ ; *manganic oxide* is  $\text{Mn}_2\text{O}_3$ . In case there are more than two oxides the number of atoms of oxygen in the molecule of the com-

pound is frequently indicated in the name. Thus *manganese dioxide* is  $\text{MnO}_2$ ; *sulphur trioxide* is  $\text{SO}_3$ ; *phosphorus pentoxide* is  $\text{P}_2\text{O}_5$ , etc. Chlorides are named in the same way. *Cuprous chloride* is  $\text{CuCl}$ ; *cupric chloride* is  $\text{CuCl}_2$ ; *ferrous chloride* is  $\text{FeCl}_2$ ; *ferric chloride* is  $\text{FeCl}_3$ ; *phosphorus trichloride* is  $\text{PCl}_3$ ; *selenium tetrachloride* is  $\text{SeCl}_4$ , etc.

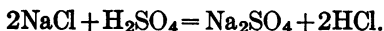
**Hydrochloric Acid,  $\text{HCl}$ .**—The only compound that chlorine and hydrogen form with each other is hydrochloric acid. It has already been shown that hydrogen burns in chlorine and that hydrochloric acid is formed. The two gases may be mixed and allowed to stand together indefinitely in the dark and no perceptible action will take place. If, however, the mixture is put in diffused sunlight, gradual combination takes place; and if the direct light of the sun is allowed to shine for an instant on the mixture, explosion occurs, and this is a sign of the combination of the two gases. The same sudden combination is effected by applying a flame or spark to the mixture, or by letting electric light or the light from a piece of burning magnesium fall upon it for an instant.

[What difference is there between the combination of hydrogen and oxygen and of hydrogen and chlorine?]

**Relation of Light to Chemical Action.**—The way in which the sunlight and other bright lights act upon the mixture of hydrogen and chlorine to cause them to combine is not understood; but the fact that sunlight does have a marked influence upon some kinds of chemical action is well known. One other illustration of this influence has already been presented, that of the decomposition of water by chlorine. This action does not take place in the dark. The sunlight

is essential. The art of photography (see Photography) is based upon the influence of light in causing chemical changes. The light from the object photographed is allowed to act in the camera on a plate, upon the surface of which is a substance that is changed chemically by light. It should be especially noted that the cause of the chemical changes in these cases is not the heat, but the light. If the substances are heated to the same temperature in the dark, the changes do not take place.

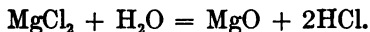
**Preparation of Hydrochloric Acid.**—To prepare hydrochloric acid, common salt or sodium chloride,  $\text{NaCl}$ , is treated with sulphuric acid (see Experiment 52, page 107). The hydrogen of the sulphuric acid and the sodium of the salt exchange places, as represented in the equation



The products are sodium sulphate and hydrochloric acid. The hydrochloric acid is given off as a gas, and the sodium sulphate remains behind in the flask.

The most convenient way to make hydrochloric acid in the laboratory is to use a Kipp's apparatus (see Fig. 13a, p. 51) filled with lumps of *fused* ammonium chloride\* and cold concentrated sulphuric acid. This yields a current of pure *dry* hydrochloric acid gas. The filled apparatus can stand for months without decomposition of the contents.

Commercially, hydrochloric acid is also now made by heating crystallized magnesium chloride:



\* Ammonium chloride can only be fused under pressure. It can be obtained from the dealers in fused form.

**Occurrence.**—Gaseous hydrochloric acid is contained in the gases escaping from volcanoes. Aqueous hydrochloric acid is an animal product; it occurs in stomach juices and is an important factor in digestion; the juices of the human stomach in normal condition contain 0.33 per cent of free hydrochloric acid.

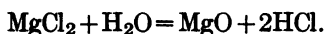
**Properties.**—Hydrochloric acid is a colorless transparent gas. It has a sharp, penetrating taste and smell. If inhaled it causes suffocation. It dissolves in water very readily. At ordinary temperatures one volume of water will dissolve 450 times its own volume of the gas. A more or less concentrated solution of the gas in water is the liquid known in the laboratory as hydrochloric acid.

[PROBLEM.—A litre of hydrochloric acid gas weighs 1.6283 grams at 0°. At 0° one volume of water will absorb 500 times its own volume of the gas. How much will a litre of water increase in weight at 0° by taking up all the hydrochloric acid it can?]

So readily does hydrochloric acid combine with water that it condenses moisture from the air; hence, although the gas itself is quite colorless and transparent, when it comes in contact with the air dense white clouds are formed, which are not formed if it is kept from contact with the air. Hydrochloric acid does not burn and does not support combustion. This is equivalent to saying that it does not combine with oxygen under ordinary circumstances, and that substances which combine with the oxygen of the air do not combine with hydrochloric acid.

[What evidence have you had that, under some circumstances, oxygen does act on hydrochloric acid? What are the circumstances? What are the products?]

**Commercial hydrochloric acid** is a yellowish liquid, the color being due to the presence of impurities. It is obtained by the action of steam on magnesium chloride:



It is also obtained as a by-product in the preparation of sodium sulphate by the action of sulphuric acid on sodium chloride.

**Pure hydrochloric acid** is a solution of the pure gas in pure water. It is colorless, and when concentrated it gives off fumes when exposed to the air. The concentrated solution when heated gives off a large part of the gas contained in it, and by boiling it can all be evaporated.

#### HYDROCHLORIC ACID.

*Experiment 57.*—Arrange an apparatus as shown in Fig. 27. The flask may be any ordinary one of about 1 litre capacity. The tubes leading into the Woulff bottles must not dip in the water in the bottles. If they end a few millimeters above the surface of the water all the gas will be absorbed.

Weigh out 5 parts common salt, 5 parts concentrated sulphuric acid, and 1 part water. Mix the acid and water, taking the usual precautions (see note bottom of page 49); let the mixture cool down to the ordinary temperature and then pour it on the salt in the flask. For the purposes of the experiment take about 50 grams of salt. Now heat the flask *gently* and the gas will be regularly evolved. What does the fact of the sinking of the solution through the water indicate?—After the gas has passed for five minutes, disconnect at *A* and let some escape into the air. Explain what you see. Blow your breath towards the end of the tube. Does this produce any effect? Explain this. Apply a lighted match to the end of the tube. Does the gas burn?—Col-

lect some of the gas in a dry cylinder by displacement of air, as in the case of chlorine. The specific gravity of the gas being 1.27 the vessel must of course be placed with the mouth upward. That

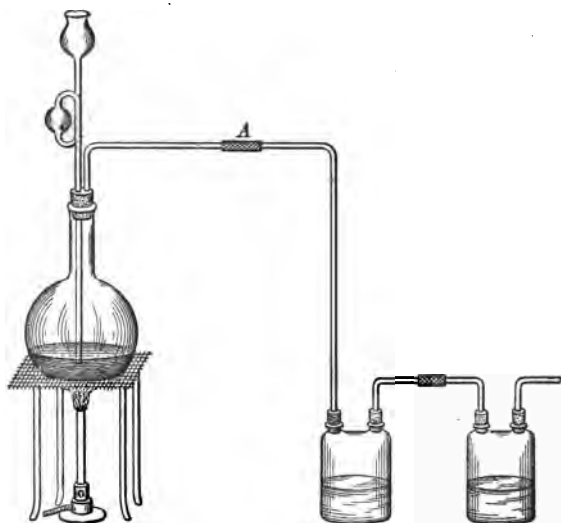
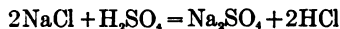


FIG. 27.

the gas is colorless and transparent is shown by the appearance of the generating-flask, which is filled with the gas. Insert a burning stick or candle in the cylinder filled with the gas. What takes place? Does the gas support combustion? Connect the generating-flask again with the two bottles containing water, and let the process continue until no more gas comes over. The reaction represented in the equation



is now complete. After the flask has cooled down, pour water on the contents; and when the substance is dissolved filter it and

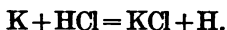


evaporate to such a concentration that, on cooling, some of the sodium sulphate is deposited. Pour off the liquid and dry the solid substance by placing it upon folds of filter-paper. Compare the substance with the common salt which you put in the flask before the experiment. What proofs have you that the two substances are not the same?—Heat a small piece of each in a dry tube closed at one end. What differences do you notice?—Treat a small piece of each in a test-tube with sulphuric acid. What difference do you notice?—If in the experiment you should recover all the sodium sulphate formed, how much would you have? Put about 5 cc. of the liquid from the first Woulff bottle in a porcelain evaporating-dish. Heat over a small flame just to boiling. Is hydrochloric acid given off?—Can all the liquid be driven off by boiling?—Try the action of the solution on some iron filings. What is given off?—Add some to a little granulated zinc in a test-tube. What is given off? Add a little to some powdered manganese dioxide in a test-tube. What is given off?—Add ten or twelve drops of the acid to 2 or 3 cc. water in a test-tube. Taste the dilute solution. How would you describe the taste? Add a drop or two of a solution of *blue* litmus, or put into it a piece of paper colored *blue* with litmus. The color is changed to *red*. Litmus is a vegetable color prepared for use as a dye. Other dyes are changed by hydrochloric acid.—Make a solution of methyl orange. Add a few drops of the solution thus obtained to dilute hydrochloric acid. Is there any change in color?—In each case add a few drops of a solution of caustic soda. What change takes place?—In what experiment has caustic soda been obtained? What relation does it bear to water?—To the dilute solution of hydrochloric acid add drop by drop a dilute solution of caustic soda. What change takes place in the taste?

**Uses.**—Hydrochloric acid is extensively used in the preparation of chlorine and of chlorides.

**Analysis of Hydrochloric Acid.**—The determination of the composition of hydrochloric acid is not as easily made as that of water. That it consists of hydrogen and chlorine

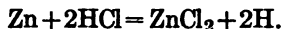
is shown by the fact that it is formed by direct combination of these elements. To determine the relative weights and volumes of the gases that enter into combination we may proceed thus: Enclose a suitable quantity of the gas in a tube. Introduce a small piece of the metal potassium. Decomposition will take place as represented in the equation



The gas left over is hydrogen. On measuring its volume it will be found to be just half that of the hydrochloric acid decomposed. The weight of the hydrogen obtained will be found to bear to the weight of the hydrochloric acid the proportion 1:36.4. In other words, in 36.4 parts of hydrochloric acid there are 35.4 parts of chlorine and 1 part of hydrogen. In 1 volume of the gas there is  $\frac{1}{2}$  volume of hydrogen. By mixing equal volumes of hydrogen and chlorine and causing them to combine it has been found that 1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrochloric acid. The specific gravity or the relative weights of equal volumes of hydrogen and chlorine are: hydrogen, 0.0696; chlorine, 2.49. These figures bear to each other very nearly the same relation as the atomic weights of the elements, viz., 1:35.4. [What fact of the same kind was noticed on comparing the specific gravities of hydrogen and oxygen?] Regarding the chemical conduct of hydrochloric acid, the experiments already performed have shown:

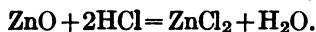
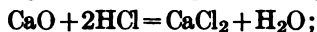
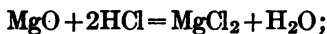
1. That hydrogen is evolved when a solution of hydrochloric acid in water is brought in contact with certain substances like iron, zinc, etc., which belong to the class called metals; and that the acid takes up the metals in place of the

hydrogen. Thus zinc and hydrochloric acid give zinc chloride and hydrogen:



2. That in contact with substances which give off oxygen, or with oxygen itself under certain circumstances, it gives up its chlorine, while the hydrogen combines with oxygen to form water.

It will be seen hereafter that when it acts upon the compounds of the metals with oxygen or the so-called metallic oxides like magnesia or magnesium oxide,  $\text{MgO}$ ; lime or calcium oxide,  $\text{CaO}$ ; zinc oxide,  $\text{ZnO}$ , etc.,—compounds which do not easily give up oxygen,—the hydrogen of the acid combines with the oxygen of the oxide to form water, while the metals combine with the chlorine:



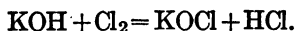
It will be noticed that when hydrochloric acid acts upon zinc oxide, zinc chloride is formed. But this is the product obtained when hydrochloric acid acts upon the metal zinc. The metals calcium and magnesium act towards hydrochloric acid the same as zinc. Plainly the cause of these reactions is the tendency on the part of chlorine to unite with the metallic elements.

**Action of Liquid Hydrochloric Acid.**—What has been said above in regard to the action of hydrochloric acid has reference to the solution of the compound in water. Liquefied hydrochloric acid does not give off its hydrogen when brought in contact with metals. The action of the water

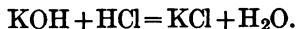
is in this case of prime importance. This subject will be discussed farther on.

**Compounds of Chlorine with Oxygen and with Hydrogen and Oxygen.**—As has been seen, chlorine combines very readily with hydrogen, and hydrogen with oxygen, and the products are stable compounds. On the other hand, chlorine cannot be made to combine directly with oxygen. By indirect processes they can be combined, but the compounds undergo decomposition easily, yielding back the chlorine and oxygen contained in them. Only a few of the more important compounds of chlorine, hydrogen, and oxygen will be taken up here.

**Compounds of Chlorine with Hydrogen and Oxygen.**—One of the principal reactions made use of for the preparation of compounds of chlorine, oxygen, and hydrogen is that which takes place when potassium hydroxide is treated with chlorine. The products are different according to the conditions. It seems not improbable that the first change is one of substitution as represented in the equation



The hydrochloric acid thus formed would not escape but would at once act upon some of the potassium hydroxide, thus



Combining the two equations we have



The compound represented by the formula  $\text{KClO}$  is *potassium hypochlorite*, while that represented by the formula  $\text{KCl}$  is potassium chloride.

If the solution of potassium hydroxide is dilute and not allowed to become hot, the change above represented is the principal one that takes place. When, however, a solution of potassium hypochlorite is heated the change represented in the following equation takes place:



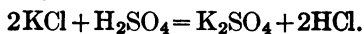
The compound represented by the formula  $\text{KClO}_3$  is *potassium chlorate*.

When chlorine is passed into a warm concentrated solution of potassium hydroxide this second change takes place. The result in this case is represented thus:

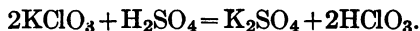


*Potassium chlorate*,  $\text{KClO}_3$ , and *potassium hypochlorite*,  $\text{KClO}$ , bear the same relation to two compounds,  $\text{HClO}_3$  and  $\text{HClO}$ , that potassium chloride,  $\text{KCl}$ , bears to hydrochloric acid,  $\text{HCl}$ , or sodium chloride,  $\text{NaCl}$ , to hydrochloric acid. But hydrochloric acid can be easily obtained from sodium chloride by adding sulphuric acid, and potassium chloride undergoes the same change when treated with sulphuric acid. Further, it will be shown later that nearly all compounds containing sodium or potassium give up these elements when treated with sulphuric acid, and take up hydrogen in their place.

On treating potassium chloride with sulphuric acid this reaction takes place:

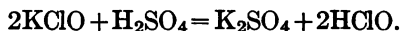


Similarly, on treating potassium chlorate with sulphuric acid, this reaction takes place:



The products are potassium sulphate and *chloric acid*,  $\text{HClO}_3$ . The chloric acid, however, is very unstable, and decomposes, yielding other compounds of chlorine. The acid itself can be made by taking proper precautions, but the chief interest connected with it is the fact that it decomposes very easily. Potassium chlorate, which is so closely related to it, is an important compound. As has been shown, it gives up its oxygen under the influence of heat. It also gives up oxygen when brought in contact with substances that have the power to unite with this element. It is a strong oxidizing agent.

*Potassium hypochlorite*,  $\text{KClO}$ , formed by passing chlorine into a dilute solution of caustic potash, is decomposed by sulphuric acid thus:



The products are potassium sulphate and *hypochlorous acid*. If a concentrated solution of potassium hypochlorite is treated with sulphuric acid, the hypochlorous acid formed at once undergoes decomposition, yielding chlorine, water, and oxygen. The acid itself is not well known. The principal compound related to it is bleaching-powder, or the substance generally known as "chloride of lime," which is familiar to every one on account of its use as a disinfecting agent. This is made by passing chlorine into slaked lime, which is similar to caustic potash. Just as when chlorine acts on a dilute solution of caustic potash a mixture of potas-

sium chloride and potassium hypochlorite is formed, so when chlorine acts on slaked lime a mixture of calcium chloride,  $\text{CaCl}_2$ , and calcium hypochlorite,  $\text{Ca}(\text{OCl})_2$ , is formed. This mixture is bleaching-powder. By treating it with an acid it gives up chlorine, and hence it affords a convenient means of transporting chlorine. Thousands of tons of this powder are manufactured annually. In making bleaching-powder chlorine is passed into the lime. The chlorine is held chemically combined until it is wanted, when it can be liberated by adding an acid or by exposure to the air.

#### PREPARATION OF POTASSIUM CHLORATE.

*Experiment 58.*—Dissolve 40 grams (or about  $1\frac{1}{4}$  ounces) caustic potash in 100 cc. water in a beaker glass, and pass into it chlorine, generated as in Experiment 53 (page 113). Use 75 grams of salt and the other reagents in proportion. Arrange an inverted funnel on the end of the delivery-tube so that the edge of the funnel dips just below the surface of the potash solution, to prevent the choking of the delivery-tube. When the solution no longer shows an alkaline reaction stop the action and boil the solution for a few minutes to expel the excess of chlorine. When the solution is allowed to cool crystals of potassium chlorate mixed with a little potassium chloride will separate out. These can be removed by filtration, and purified by recrystallization from a small amount of water. This solution should be filtered before it becomes cool enough to deposit the crystals. Filter off the crystals and dry them. Is the substance potassium chlorate? Does it give off oxygen when heated? In a dry test-tube pour a drop or two of concentrated sulphuric acid on a small crystal of it. Do the same with a piece of potassium chlorate not larger than a grain of rice. Hold the mouth of the test-tube away from the face as with potassium chlorate the action is explosive. What is noticed in each case?—Evaporate the solution from which the potassium chlorate was originally obtained to half its volume

and, after cooling, filter off any substance that may be deposited. Evaporate the filtrate to dryness. Does this substance give off oxygen when heated? Does it give off a gas when treated with sulphuric acid? Is this gas colored? If the gas is hydrochloric acid, what is the solid substance from which it is formed? And what is left in the test-tube?

#### PREPARATION OF BLEACHING-POWDER.

*Experiment 59.*—Place the slaked lime, made by slaking 20 to 30 grams of quick-lime with enough hot water to make a dry

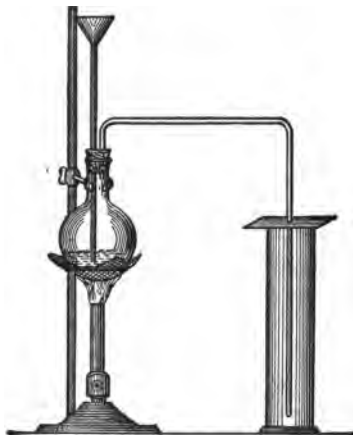


FIG. 28.

powder, in a 250-cc. flask with a two-hole stopper. Introduce a glass tube through one of the holes and pass chlorine in slowly, keeping the flask thoroughly agitated, for about ten minutes. Introduce a funnel and delivery-tube as shown in Fig. 28. Pour a mixture of equal parts of sulphuric acid and water slowly through the funnel-tube. Collect by displacement of air the gas given off. What evidence have you that the gas is chlorine?

**Decomposition of Bleaching-powder by Acids.**—In the last experiment the substance first formed is bleaching-



powder, or "chloride of lime" (see page 128). This is decomposed by sulphuric acid, yielding chlorine. The formation of chlorine is secondary, and due to the ease with which hypochlorous acid breaks up into chlorine, oxygen, and water.

**Other Compounds of Chlorine, Hydrogen, and Oxygen.—**

While the remaining compounds of chlorine, hydrogen, and oxygen cannot be treated of here in detail, a reference to the series as a whole will serve to call to mind some important matters of general interest. There are four of these compounds which, so far as composition is concerned, bear a very simple relation to one another. They are *hypochlorous acid*,  $\text{HClO}$ ; *chlorous acid*,  $\text{HClO}_2$ ; *chloric acid*,  $\text{HClO}_3$ ; and *perchloric acid*,  $\text{HClO}_4$ . Beginning with hydrochloric acid, we have thus a series of compounds, the successive members of which differ by one atom of oxygen:

Hydrochloric acid. . . . .	$\text{HCl}$
Hypochlorous acid. . . . .	$\text{HClO}$
Chlorous acid. . . . .	$\text{HClO}_2$
Chloric acid. . . . .	$\text{HClO}_3$
Perchloric acid. . . . .	$\text{HClO}_4$

This series illustrates very clearly the *law of multiple proportions* (see page 83). [What is the law of multiple proportions? How does this series illustrate the law?]

## CHAPTER VIII.

### ELECTROLYSIS.—ACIDS.—BASES.—NEUTRALIZATION.— SALTS.

#### ELECTROLYSIS.

**Electric Current.**—By galvanic batteries, by dynamos, and by other methods a condition can be produced in conductors of electricity which is called an *electric current*. This current can perform mechanical work, cause chemical change, develop heat, etc.; it is therefore a form of energy.

**Conductors.**—Some substances conduct the electric current, others do not. Metals are conductors. Non-metallic elements generally are not. There are two classes of conductors. The metals are in the first class. Such conductors are heated but not otherwise changed by the passage of the current. Conductors of the second class are chemically changed by the passage of the current, their components being chemically separated at the points where they are in contact with the electrodes or metallic conductors of the current from the battery. Aqueous solutions of acids, bases and salts are conductors of the second class at ordinary temperature. These substances, in the absence of water, do not conduct the current or are very poor conductors. If they are solid, however, they become conductors when fused.

**Electrolysis.**—The phenomenon of decomposition by the electric current is called *electrolysis*. The conductors of the second class are called *electrolytes*. The metallic ends of the electric circuit which come in contact with the electrolyte are called *electrodes*.

Water does not conduct electricity.\* That this is so, and that solutions of acids, bases and salts in water are conductors may be proved by a simple experiment.

**EXPERIMENT 59a.**—Bring an electric bell into the circuit from a battery. The wire leading from the bell ends in a platinum electrode; this electrode and another fastened to the end of the second wire from the battery dip into a beaker glass as shown in Fig. 28a.

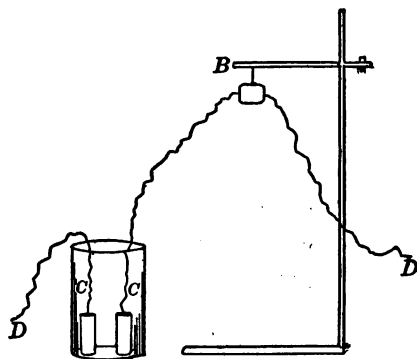


FIG. 28a.

Turn on the current and bring the electrodes together; this completes the circuit, and the bell rings. Separate the electrodes; the bell stops ringing. Pour pure water into the beaker so that the electrodes dip into it; the bell does not ring.

\* This is not absolutely true; but a column of water one centimeter in diameter and one centimeter high does not conduct as well as would a column of mercury of the same diameter and one million kilometers high.

Pour hydrochloric acid into the water; the bell rings and bubbles of gas escape from the electrodes.

Wash out the beaker and repeat the experiment with the solution of sodium chloride in the beaker. Repeat again with a solution of sodium hydroxide in the beaker.

Repeat the experiment with a solution of copper sulphate in the beaker. Note the deposit of metallic copper on the *cathode*.

Repeat the experiment with a solution of silver nitrate in the beaker. Note the deposit of silver on the cathode.

The molecule is the unit of matter. In the decomposition of electrolytes their molecules are broken down into smaller units which may contain one or more than one atom. These units are called *ions*. The dissociation of molecules into ions is called *ionisation*.

**Anions and Cations.**—A study of electrolysis shows that the hydrogen of acids always collects at the *negative* electrode, that is, the electrode at which the positive electric current leaves the electrolyte to pass into the metallic circuit. The metal of salts and the metal of bases appears at the same electrode. The ions which move to the negative electrode are called *cations* and the electrode is called the cathode. Hydrogen is the cation of acids, the cations of bases and salts are the metals.

In the electrolysis of hydrochloric acid or of a metallic chloride, the chlorine is found at the positive electrode. Ions which collect at the positive electrode are called *anions*, and the electrode is called the anode.

**Faraday's First Law.**—Faraday (1833) experimentally proved the facts which are expressed in the law: *The amount of matter which is discharged at the electrodes in a*

*given time is strictly proportional to the strength of the electric current passing through the electrolyte.* Hence it is believed that passage of the electricity through the electrolytes depends on the simultaneous movement of the ions, so that there can be no passage of the electric current unless the ions carry it.

Ions are conceived as matter charged with electricity while the same matter in its ordinary state is not charged with electricity; hence the ion of a substance differs from the non-ionised substance by the electric energy of its charge.

**Faraday's Second Law.**—It has been shown that in the electrolysis of hydrochloric acid the hydrochloric acid molecule,  $\text{HCl}$ , dissociates into hydrogen cation and chlorine anion which are written thus  $\text{H}^+$ ,  $\text{Cl}^-$ , the plus sign denoting cations, the minus sign, anions. As the hydrogen ion carries a definite charge of positive electricity, the chlorine ion must carry *an equal charge* of negative electricity. As the atomic weight of hydrogen is 1 and that of chlorine 35.4, and as the molecule of hydrochloric acid,  $\text{HCl}$ , is made up of one atom of hydrogen and one of chlorine, it follows that if 1 gram hydrogen carries a certain positive charge, 35.4 grams chlorine carry an equal negative charge of 96540 coulombs. This is expressed by Faraday as follows. *The amounts of the different elements which are separated by electricity bear the same relation to one another as the equivalents of the elements.*

Hence if 1 gram of hydrogen when ionised and 35.4 grams chlorine each carries an equal charge, 23 grams of sodium ionised carries the same.

If we assume as unit the amount or *charge* of electricity carried by *one hydrogen ion*, it follows that the chlorine ion carries one charge and the sodium ion also one charge. Calcium chloride has the composition  $\text{CaCl}_2$ ; when the molecule  $\text{CaCl}_2$  is ionised it gives the ions  $\text{Ca}^+$ ,  $\text{Cl}^-$ ,  $\text{Cl}^-$ . Each chlorine ion carries one charge of negative electricity, hence the calcium ion must carry two charges of positive electricity.

Hence in the ionisation of salts the ion of a univalent metal carries one charge, the ion of a bivalent metal two charges, the ion of a trivalent metal three charges.

**Primary and Secondary Products of Electrolysis.**—When very dilute hydrochloric acid is ionised hydrogen is given off at the cathode, but no chlorine at the anode. In its place an equivalent amount of oxygen is given off. This is due to the fact that the water is decomposed by the chlorine:  $2\text{H}_2\text{O} + 4\text{Cl} = 4\text{HCl} + \text{O}_2$ . The hydrogen and chlorine are *primary products*, oxygen a *secondary product* of electrolysis.

Such secondary products are often formed when the substance first given off is not stable under existing conditions.

In the electrolysis of copper or silver salts, copper or silver is obtained at the cathode; they are primary products; but if sodium chloride is electrolyzed hydrogen is given off at the cathode. This is due to the fact that the primary product, sodium, acts on the water forming sodium hydroxide, which dissolves in the water, and hydrogen, which escapes.

EXPERIMENT 59*b*.—Instead of the beaker used in the last experiment use the apparatus shown in diagram Fig. 31. It consists of two glass tubes about  $\frac{3}{4}$  inch diameter and 5 inches long, connected 2 inches from the bottom by a short

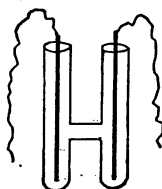
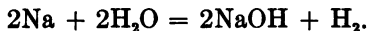


FIG. 28*b*.

piece of tube about  $\frac{1}{4}$  inch inside diameter. Let thin platinum wires ending in narrow strips of platinum foil as electrodes dip into the tubes as shown. Connect with the wires from the battery. Make a concentrated solution of sodium chloride in water; add enough red litmus solution to give it a pink tinge. Pour the solution into the apparatus until it reaches just above the cross-piece. Turn on the current. The liquid over the cathode will turn blue, indicating the presence of a dissolved base (sodium hydroxide); hydrogen escapes. The liquid over the anode will become colorless owing to the bleaching action of the chlorine. The odor of chlorine is also noticeable.

When a solution of sodium hydroxide, NaOH, is electrolyzed, hydrogen is given off at the cathode for the above reason, and oxygen at the anode. The ions of sodium hydroxide are  $\text{Na}^+$  and  $\text{OH}^-$ , the primary anode product is hydroxyl, OH; this cannot be isolated on account of its instability, and the reaction  $4\text{OH} = 2\text{H}_2\text{O} + \text{O}_2$  occurs, the secondary product, oxygen, being actually given off.

If in the electrolysis of sodium chloride or of sodium hydroxide, the platinum cathode is replaced by a mercury cathode, no hydrogen escapes as the sodium dissolves in the mercury. If the solution of sodium in mercury is put into pure water, hydrogen escapes and the water becomes alkaline:



**EXPERIMENT 59c.**—Instead of the beaker used in Exp. 59a, take a piece of glass tubing  $\frac{3}{4}$  inch inside diameter and 4 or 5 inches long. Close one end with a cork, through which the sharpened end of the *cathode* wire has been pushed so that it projects  $\frac{1}{2}$  inch into the tube. Fasten the tube by a clamp in the vertical position with the cork at the bottom. Pour mercury into the tube to the depth of  $\frac{3}{4}$  inch. Introduce the anode into the upper part of the tube. Pour in some of the same concentrated solution of sodium chloride colored with red litmus as that used in the last experiment. Turn on the current. Chlorine is given off, bleaching the litmus at the anode, but no hydrogen escapes, and no sodium hydroxide is formed. After a few moments shut off the current; pour off as much of the liquid in the tube as you can without losing mercury. Pour the mercury into the dish, remove the remainder of the solution of salt by absorbing with filter paper, add pure water. Hydrogen escapes slowly as the sodium amalgam\* decomposes. Add a drop of red litmus. The solution turns blue.

**Commercial Methods for the Electrolysis of Sodium Chloride.**—The products of the commercial electrolysis of sodium chloride are chlorine, sodium hydroxide, and hydrogen generally, though, by a modification of the process, *both* of the primary products, sodium and chlorine, are obtained (see SODIUM).

That the electrolytic process for the preparation of chlorine on the large scale has come into extensive use is shown by the following table which gives the percentage of chlorine made electrolytically and by the chemical process in different countries in 1905.

\* The alloys of mercury with other metals, i.e., the solution of other metals in mercury, are called *amalgams*.



	Electrolytic.	Chemical.
United States.....	100.....	—
Germany.....	65.....	35
Great Britain.....	18.....	82
France.....	19.....	81
Austria.....	66.....	34
Spain and Italy.....	100.....	—
Russia.....	55.....	45
Belgium.....	54.....	46

Cheap electric-power is the chief factor in the introduction of electrolytic processes. Regions where there is plentiful water-power are becoming the seats of such industries.

**Neutralization.**—It is now time to inquire what features acids have in common that lead chemists to give them that name. It is not possible to understand the nature of their common properties without a reference to a class of substances to which special attention will be called in due time. These are the *alkalies*, which are the most marked representatives of the class of substances known as *bases*. These two classes, the *acids* and the *bases*, have the power to destroy the characteristic properties of each other. When an acid is brought in contact with a base in proper proportions, the characteristic properties of both the acid and the base are destroyed. They are said to *neutralize* each other. This act of neutralization is a very important one, with which we constantly have to deal in chemical operations.

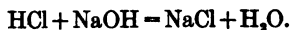
**Litmus Test for Acids and Alkalies.**—The most common acids are sulphuric, hydrochloric, and nitric acids. Among the more common bases are caustic soda, caustic potash,

and lime. A convenient way to recognize whether a substance has acid or basic properties is by means of certain color-changes. The dye litmus is blue. If a solution that is colored blue with litmus is treated with a drop of an acid, the color is changed to red. If now the red solution is treated with a drop or two of a solution of a base, the blue color is restored. There are many other substances which have markedly different colors in acid and in alkaline solutions.

**What is Formed when an Acid and a Base Neutralize Each Other?**—Experiment alone can answer. A few such examples as those below will be helpful.

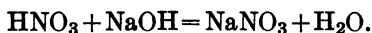
#### NEUTRALIZATION.

*Experiment 60.*—Dissolve 5 grams caustic soda in 100 cc. water. Dilute the hydrochloric acid found in the bottle in the laboratory by adding 30–40 cc. of it to an equal volume of water. Add this diluted acid slowly to the solution of caustic soda, testing the liquid from time to time by means of a piece of blue litmus paper. As long as the solution is alkaline it will cause no change in the color of the paper. The instant it passes the point of neutrality and becomes acid the paper will turn red; when exactly neutral it will neither change the blue to red, nor, if the color of the paper is changed to red by means of another acid, will it turn it blue again. When this point is reached, evaporate off the water on the water-bath to *complete dryness* and see what is left. Taste the substance. Has it an acid taste? Does it suggest any familiar substance? If it is sodium chloride, how ought it to conduct itself when treated with sulphuric acid? Does it conduct itself in this way? Satisfactory evidence can be given that the substance is sodium chloride. It is not an acid nor an alkali. It is neutral. Its formation took place according to the equation

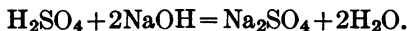


*Experiment 61.* — Perform a similar experiment using nitric acid and caustic soda. The product formed is sodium nitrate. Compare it with sodium nitrate from the laboratory bottle. Heat a small specimen of each in a tube closed at one end. What do you observe? Treat a small specimen of each with a little sulphuric acid in test-tubes. What do you observe?

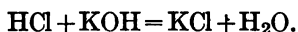
**The Reactions.** — The explanation of the changes that occur in these cases will be given later. Here the point to be noted is, that the substance formed when nitric acid acts on caustic soda is sodium nitrate. The reaction takes place thus:



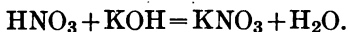
Similarly sulphuric acid and caustic soda give sodium sulphate and water, thus:



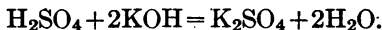
With caustic potash similar reactions take place. Hydrochloric acid and caustic potash yield potassium chloride and water:



Nitric acid and caustic potash yield potassium nitrate and water:



Sulphuric acid and caustic potash yield potassium sulphate and water:



By reference to the foregoing equations it will be seen:

(1) That an acid contains hydrogen;

(2) That a base contains a so-called metallic element in combination with hydrogen and oxygen;

(3) That when an acid acts upon a base the hydrogen of the acid combines with the hydrogen and oxygen of the base to form water. The result is that the hydrogen of the acid and the metallic element of the base exchange places;

(4) That the substance formed from the acid by substituting a metallic element for the hydrogen is neutral.

These statements are of general application, except statement (4), to which there are some exceptions. It is true in some cases that after replacing the hydrogen the substance has an alkaline reaction, and in other cases that the product has an acid reaction.

It has been shown that hydrochloric acid and sulphuric acid act upon certain metals, as iron and zinc, and that the action consists in giving up hydrogen and taking up metal in its place. The products of this kind of action are the same in character as those formed by the action of acids on bases.

**Gram-molecular Weights.**—By this term is designated the molecular weight of a compound expressed in grams. Thus hydrochloric acid has the molecular weight 36.4, and 36.4 grams of hydrochloric acid gas is one *gram-molecular weight*, abbreviated to gr. mol. wt.

From the above equations it follows that if we prepare aqueous solutions of hydrochloric acid, nitric acid, potassium hydroxide, and sodium hydroxide in which one liter of solution contains one gr. mol. wt. of the respective substances, equal volumes of the solutions of either one of the

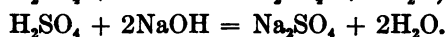
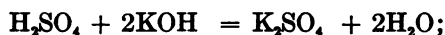
acids must exactly neutralize the same volumes of the solutions of either of the bases.

Mol. wt. HCl, 36.4; HNO<sub>3</sub>, 63; KOH, 56; NaOH, 40.

The solution of

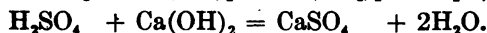
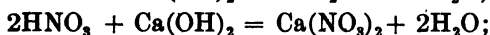
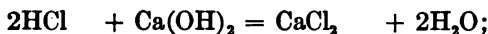
HCl	contains in the liter	1	gram	H	and 35.4	gram	Cl
HNO <sub>3</sub>	" " " "	1	"	H	"	62	" NO <sub>3</sub>
KOH	" " " "	17	grams	OH	"	39	" K
NaOH	" " " "	17	"	OH	"	23	" Na

Sulphuric acid acts upon these same bases thus:



From these equations it is evident that it would require 2 liters of the above-mentioned solutions of either of the bases to neutralize 1 liter of an aqueous solution of sulphuric acid, containing one gr. mol. wt. H<sub>2</sub>SO<sub>4</sub> (mol. wt. H<sub>2</sub>SO<sub>4</sub>, 98. One gr. mol. wt. sulphuric acid contains 2 gr. H). It is also evident that  $\frac{2}{98}$  grams sulphuric acid diluted with water to one liter would contain 1 gram hydrogen, and that a given volume of this solution must exactly neutralize the same volume of either of the above-mentioned solutions of bases.

The neutralization of calcium hydroxide by acids is represented thus:



Mol. wt.  $\text{Ca(OH)}_2 = 74$ . One gr. mol. wt. contains 34 grams of OH. By reasoning similar to that in the preceding paragraph, it is evident that if we made an aqueous solution of calcium hydroxide containing  $\frac{1}{2}$  grams of calcium hydroxide,  $\text{Ca(OH)}_2$ , in one liter, any volume of this solution would exactly neutralize an equal volume of the solutions of nitric acid or hydrochloric acid or of the solution of sulphuric acid containing  $\frac{1}{2}$  grams sulphuric acid,  $\text{H}_2\text{SO}_4$ , in the liter.

What have these equations in common? In each case 1 gram hydrogen has combined with 17 grams hydroxyl, OH, to form water.

**Importance of Water in the Experiments on Neutralization.**—One fact of great importance is not taken into consideration in what has thus far been said concerning neutralization. It is this: *The substances must be brought together in solution.* Dry hydrochloric acid and dry potassium hydroxide, for example, do not act upon each other, and the same is true of other perfectly dry acids and bases. *Water is essential to the action.* This raises the question:

**What is Solution?**—No satisfactory answer can yet be given to this question. There are many liquids besides water in which solids can be dissolved, but for the present attention may be confined to solutions in water. Of these two kinds can be distinguished between:

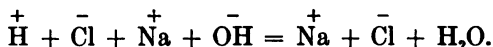
- (1) The solutions of some substances conduct electricity;
- (2) The solutions of other substances do not conduct electricity.

Substances of the first class are called *electrolytes*. To this class belong acids, bases, and salts.

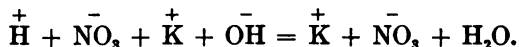
Substances of the second class are called *non-electrolytes*. To this class belong sugar and many other compounds less familiar.

**Electrolytic Dissociation.**—It has been shown that a very weak electric current acting upon a solution of an electrolyte is sufficient to cause the *ions* to appear at the poles. This fact is inexplicable if it is assumed that the current is the cause of the decomposition of the electrolyte. This, and some other facts, make it probable that electrolytes are at least to some extent decomposed into their constituent *ions* when they are dissolved in water; that these ions charged with electricity transfer their charges in the solution and thus conduct the current; and that when an ion charged with negative electricity reaches the positive pole its electricity is discharged, and the ion then ceases to be an ion and becomes an element in the free state or some compound which appears either as such or in the form of other products. According to this conception, *the act of solution of an electrolyte, in water at least, involves partial breaking down or dissociation of the compound into its ions*. The extent of this breaking down is determined primarily by the concentration of the solution—the greater the dilution the greater the dissociation. At infinite dilution there is complete dissociation. A water solution of hydrochloric acid containing 36.4 grams of the acid in 1000 liters has been shown to be completely dissociated, or it is to be regarded as containing only hydrogen ions and chlorine ions. These and all other ions are carefully to be distinguished from the atoms or definite compounds. An ion always carries with it a certain charge of electricity. When this is discharged

the ion becomes either an element or a compound in the free state. When a solution of one electrolyte acts upon a solution of another the reaction observed is probably due to the interaction of the ions, and it is further probable that, so far as the compounds are present in the undissociated condition, they do not act upon each other. When, for example, an acid acts upon a base in solution it appears that, so far as they react, they are in dissociated condition. Thus hydrochloric acid and sodium hydroxide are to be regarded as acting as represented in the following equation:



The act consists in the union of the hydroxyl ion of the base with the hydrogen ion of the acid to form water, the sodium and chlorine ions remaining as ions. In the case of nitric acid and potassium hydroxide the following equation represents the reaction at infinite dilution:



And so also whenever the act of neutralization takes place there is simply a union of hydrogen ions with hydroxyl ions to form water.

This conception finds strong confirmation in the fact that the heat evolved in neutralizing equivalent quantities of all acids at infinite dilution is always the same—a fact difficult to explain if it is assumed that in the act of neutralization a salt is formed in the solution, but this fact is easily understood, if the act of neutralization consists in the union of a hydroxyl ion with a hydrogen ion to form water.



Thus it appears that the formation of water is not only the action common to every act of neutralization of an acid by a base, but it is the only action occurring at great dilutions. If the neutralized solution is evaporated and the water driven off, the number of ions decreases as molecules of the salt are formed in the concentrated solution. When all the water is evaporated practically no ions are present, as dry salts do not conduct electricity at ordinary temperatures.

**Normal Solutions.**—Aqueous solutions of acids containing 1 gram hydrogen in the liter are called *normal solutions*, or *N-solutions*. Aqueous solutions of bases containing 17 grams hydroxyl in the liter are called *normal solutions* of bases (see p. 159). One-tenth normal solutions of acids ( $N/10$ ) contain 0.1 gram ionisable hydrogen in the liter;  $N/10$ -solutions of bases contain 0.17 gram hydroxyl in the liter.

**Definition of Acids and Bases in Terms of the Theory of Electrolytic Dissociation.**—If the views above presented are correct, and the evidence upon which they rest is undoubtedly strong, then acids and bases should be defined as follows:

(1) An acid is a substance that gives hydrogen ions when dissolved in water;\*

(2) A base is a substance that gives ions of the composition represented by the formula  $\text{OH}$ , called *hydroxyl*, when dissolved in water.

The common properties of acids—the sour taste, the evolution of hydrogen when brought together with metals,

\* Some other solvents act like water, but not in so marked a way.

their action on dyes, their power to neutralize bases—are believed to be due to the fact that they all give hydrogen ions.

So also the common properties of bases—their alkaline taste, their action on dyes, their power to neutralize acids—are believed to be due to the fact that they give hydroxyl ions.

**Salts.**—When an acid and a base are brought together, then, water is the first product of the action. The other product is called a *salt*. Thus sodium chloride,  $\text{NaCl}$ , potassium nitrate,  $\text{KNO}_3$ , potassium chloride,  $\text{KCl}$ , etc., are called salts. Comparing these salts with the acids from which they are derived, it will be seen that they are formed from these by the substitution of the elements sodium and potassium for the hydrogen of the acids:



Sodium and potassium are examples of a class of elements that are called metallic elements. Speaking broadly, a salt is a substance formed by substituting a metallic element for the hydrogen of an acid.

**Metallic Elements.**—It may fairly be asked, What is a metallic element? Unfortunately for our present purpose, it is by no means easy to give a satisfactory answer to this question. Examples of metals can easily be given, such as iron, zinc, silver, calcium, magnesium, etc.; but when the attempt is made to state what the distinguishing features

of these substances are, difficulties are met with. In general it may be said that to the chemist any element is metallic which when combined with hydrogen and oxygen forms a product that has the power to neutralize acids; that is to say, that has basic properties. In general, any element that has the power to enter into an acid in place of the hydrogen is called a metal, or is said to have metallic properties. This is the sense in which the word metal is used in this book.

**Nomenclature of Acids.**—The names of those acids of chlorine which contain oxygen illustrate some of the principles of nomenclature in use in chemistry. That acid of the series which is best known is called chloric acid. The termination *ic* is generally used in naming acids, as is seen in the names hydrochloric, sulphuric, nitric, etc. If a second acid containing the same elements exists and the proportion of oxygen contained in it is smaller than in the acid the name of which ends in *ic*, the second acid is given a name ending in *ous*. Thus *chlorous* acid contains a smaller proportion of oxygen than *chloric* acid, and the suffixes *ic* and *ous* signify that fact. There are many other examples of this use of these suffixes in the names of acids as well as in the names of compounds of other classes.

In the series of chlorine acids, however, this simple principle, which is sufficient for most cases, does not suffice. In order, therefore, to form characteristic names for the other members of the series recourse is had to prefixes. There is one acid which, so far as the proportion of oxygen contained in it is concerned, stands below chlorous acid. It is called *hypochlorous* acid, the prefix *hypo* being derived from the Greek ὑπό, under. Further, there is an acid

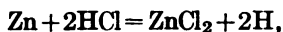
which contains a larger proportion of oxygen than chloric acid. It is called *perchloric acid*, the Latin prefix *per* signifying here *very* or *fully*. It will be seen that the names of the acids vary with the proportion of oxygen contained in them.

**Nomenclature of Bases.**—As pointed out above, a base is a compound of a metal with hydrogen and oxygen or with hydroxyl. Thus, caustic soda has the formula  $\text{NaOH}$ , caustic potash  $\text{KOH}$ , lime  $\text{CaO}_2\text{H}_2$ , etc. They are commonly known as hydroxides. In order to distinguish between the hydroxides of the different metals, the names of the metals are put before the name hydroxide. Thus, caustic soda,  $\text{NaOH}$ , is called *sodium hydroxide*; caustic potash,  $\text{KOH}$ , is called *potassium hydroxide*; caustic lime,  $\text{CaO}_2\text{H}_2$ , is called *calcium hydroxide*, etc. They are regarded as water in which a part of the hydrogen has been replaced by a metal, and indeed many of them can be made by simply bringing the corresponding metals in contact with water. Thus, as has been seen (Exp. 27, page 45), when sodium or potassium is thrown on water hydrogen is evolved. The products formed are, respectively, sodium hydroxide and potassium hydroxide. These compounds are called *hydrates* by some chemists, the name implying that they are derivatives of water. The name hydroxide means simply that the substances contain hydrogen and oxygen.

**Nomenclature of Salts.**—Theoretically every metal can yield a salt with every acid. The salts derived from a given acid receive a general name, and this general name is qualified in each case by the name of the metal contained in the salt. Thus all the salts derived from nitric acid

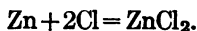
are called *nitrates*; all the salts derived from chloric acid are called *chlorates*; the salts of sulphuric acid are called *sulphates*.\* So too, further, the salts of chlorous acid are called *chlorites*; those of nitrous acid, *nitrites*; those of sulphurous acid, *sulphites*, etc., etc. It will be noticed that the terminal syllable of the name of the salt differs according to the name of the acid. If the name of the acid ends in *ic*, the name of the salt derived from it ends in *ate*. If the name of the acid ends in *ous*, the name of the salt ends in *ite*. To distinguish between the different salts of the same acid, the name of the metal contained in it is prefixed. Thus, the potassium salt of nitric acid is called potassium nitrate, the sodium salt is called sodium nitrate; the calcium salt of sulphuric acid is called calcium sulphate; the magnesium salt of nitrous acid is magnesium nitrite. The calcium salt of hypochlorous acid is calcium hypochlorite, etc., etc. [Give the name and formula of the potassium salt of perchloric acid.—Give the name and formula of the sodium salt of hypochlorous acid.—Give the name and formula of the sodium salt of chlorous acid.]

If the salts of hydrochloric acid were named in accordance with the principle just explained, they would be called *hydrochlorates*. But it will be observed that these salts are identical with the products formed by direct combination of the metals with chlorine (see page 117). Thus, hydrochloric acid and zinc act as represented in the equation



\* If the principle were strictly applied the salts of sulphuric acid would be called *sulphurates*, but for the sake of convenience the name is shortened.

while zinc and chlorine act thus:



In each case the same product,  $\text{ZnCl}_2$ , is formed. But these compounds of metals with chlorine are called *chlorides*, as has already been explained. Hence the name *hydrochlorate* is unnecessary.

**Acid Properties and Oxygen.**—The observation that oxygen is generally present in acids led at one time to the belief that it is an essential constituent of these substances. Hence the name oxygen was given to it (from *ὀξύς*, acid, and *γεννάω*, I form). That oxygen is not essential to the existence of acid properties is shown in the case of hydrochloric acid, and in a few other similar cases. Hydrogen is the element that is essential to acids, but not all hydrogen compounds are acids, as shown, for example, by the bases which contain hydrogen.

**Summary.**—When acids and bases are brought together in solution in certain definite proportions they destroy each other's characteristic properties or they neutralize each other.

An acid contains hydrogen.

A base contains hydrogen and oxygen or hydroxyl (OH).

When an acid acts upon a base, water and a salt are formed.

It is essential to many chemical reactions that the substances that are brought together should be in solution in water.

It is believed that acids, bases, and salts are decomposed (dissociated) into *ions* when dissolved in water, acids giving hydrogen ions, and bases giving hydroxyl ions.

Neutralization, according to this, consists essentially in the union of hydrogen ions with hydroxyl ions to form water.

A salt is a substance formed by substituting a metallic element for the hydrogen of an acid.

Any element that has the power to enter into an acid in place of the hydrogen is called a metallic element.

Acids receive names according to the relative quantity of oxygen contained in them.

Bases are generally called hydroxides.

Salts are named according to the names of the acids and the bases from which they are formed.

The name oxygen, meaning acid-former, is not justified.

## CHAPTER IX.

### NITROGEN.—AIR.

**Two Gases in the Air.**—It has been stated that when substances burn in the air the same products are formed as when they burn in oxygen; and, further, that there is something besides oxygen present in the air which renders the burning less active than it is in oxygen alone. When phosphorus is exposed to the air it combines slowly with oxygen, and the phosphorus pentoxide formed easily dissolves in water. These facts may be utilized for the purpose of getting possession of the other gas in the air, as this does not combine with phosphorus.

**Quantitative Study of the Composition of the Air.**—The proportion of oxygen to nitrogen in the air can be determined as below.

#### ANALYSIS OF AIR.

*Experiment 62.*—Arrange an apparatus as in Fig. 29. Use a tube graduated in cubic centimetres. Enclose 60 to 80 cc. air in the tube over water. Arrange the tube so that the level of the water inside and outside is the same. Note the temperature of the air and the height of the barometer. Reduce the observed volume to standard conditions. Now introduce a piece of phosphorus fastened to the end of the wire by winding the wire around it, and allow it to stand for twenty-four hours. Draw out the phos-



phorus and leave it under water in the cylinder. Again arrange the tube so that the level of the water inside is the same as that outside. Make the necessary corrections for temperature, pressure, and pressure of water-vapor. It will be found that the volume has diminished considerably, but that about four fifths of the gas originally put in the tube is still there. If the work is done carefully, the volume of the gas left in the tube will be to the total volume used as 79 to 100. In other words, of every 100 cc. air used 21 cc. are absorbed by phosphorus, and 79 cc. are not. The experiment should be repeated two or three times and the results compared. The gas absorbed is oxygen, identical with the oxygen made from the oxide of mercury, manganese dioxide, and potassium chlorate. Carefully take the tube out of the vessel of water, closing its mouth with the thumb or some other suitable object to prevent the contents from escaping. Turn it with the mouth upward, and introduce into it a burning stick. What takes place?

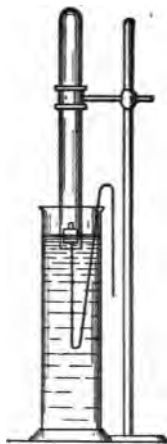
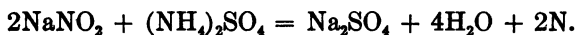


FIG. 29.

**Nitrogen.**—The experiment just performed shows us that the air is made up by volume of 21 per cent of oxygen and 79 per cent of a gas that does not support combustion. This second constituent of the air is *nitrogen*.

**Preparation.**—Anything that has the power to absorb oxygen may be used in the preparation of nitrogen from the air. To avoid contamination of the nitrogen with other substances, however, it is necessary to use something which does not form a gaseous product when burned. Metallic copper is convenient, and is often used. It is only necessary to pass air over heated copper, when the metal com-

biner with oxygen, forming the solid copper oxide,  $\text{CuO}$ , leaving the nitrogen uncombined. A convenient way to prepare nitrogen is to burn a piece of phosphorus in a bell-jar over water. The simplest method of obtaining pure nitrogen practically is to heat a concentrated solution of ammonium sulphate mixed with a solution of sodium nitrite, passing the nitrogen generated through a wash-bottle filled with potassium bichromate and dilute sulphuric acid which removes accidental impurities:



#### NITROGEN.

*Experiment 66.*—Place a good-sized stoppered bell-jar over water in a pneumatic trough. Float a small porcelain dish about 2 in. in diameter on the water in the trough. Put into it a piece of phosphorus about twice the size of a pea, and set fire to it. Quickly place the bell-jar over it. At first some air will be driven out of the jar. [Why?] The burning will continue for a short time, and then gradually grow less and less active, finally stopping. On cooling, it will be found that the volume of gas is less than four fifths the original volume, for the reason that some of the air was driven out of the vessel at the beginning of the experiment. Before removing the stopper of the bell-jar see that the level of the liquid outside is the same as that inside. Try the effect of introducing successively several burning bodies into the nitrogen,—as, for example, a candle, a piece of sulphur, phosphorus, etc.

**The Air.**—The nitrogen and oxygen which make up the air are not chemically combined with each other, but simply mixed together. It is not an easy matter to prove this statement, but the evidence is so strong that no chemist doubts it.

(1) If nitrogen and oxygen are mixed together, the mix-

ture conducts itself in many respects, for example, in combustion, the same as air.

(2) When nitrogen and oxygen are mixed the mixing is not accompanied by any phenomena indicating chemical action. Generally, the chemical union of two substances is accompanied by a change in their temperature. When nitrogen and oxygen are mixed there is no change in the temperature of the gases.

(3) The composition of a chemical compound is constant. The law of definite proportions is founded upon a very large number of observations, and in all cases in which there is independent evidence that chemical action takes place, it is found that the same substances combine in the same proportions to form the same product. Variation in the composition of a chemical compound is not known. The composition of the air varies slightly, according to circumstances.

(4) Air dissolves somewhat in water. If air which has been thus dissolved is pumped out and analyzed, it is found to have a composition different from that of ordinary air. Instead of containing 1 volume of oxygen to 4 volumes of nitrogen, it contains 1 volume of oxygen to 1.87 volumes of nitrogen. The relative quantity of the oxygen is much larger in air that has been dissolved in water than it is in ordinary air. This is due to the fact that oxygen is more soluble in water than nitrogen is. In order, however, that one gas may dissolve more than the other, it is necessary that they should not be in chemical combination. If they were in chemical combination the compound as such would probably dissolve if anything dissolved.

**Occurrence of Nitrogen.**—Besides being found uncombined in the air, nitrogen is found in combination in a large number of substances in nature. It is found in the nitrates, or salts of nitric acid, particularly as the potassium salt,  $\text{KNO}_3$ , known as saltpetre, and the sodium salt,  $\text{NaNO}_3$ , known as Chili saltpetre. It is also found in the form of ammonia, which is a compound of nitrogen and hydrogen represented by the formula  $\text{NH}_3$ . Ammonia occurs in small quantity in the air, and is formed under a variety of conditions, to which reference will be made when the substance is presented. Nitrogen occurs, further, in most animal substances in chemical combination.

**Properties of Nitrogen.**—It has been seen that nitrogen is a colorless, tasteless, inodorous gas. It does not support combustion, nor does it burn. (Suppose nitrogen were combustible, what would be the composition of the atmosphere?) Nitrogen not only does not combine directly with oxygen readily, but it does not combine directly with any other element except at very high temperature. Just as it does not support combustion, so also it does not support respiration. An animal would die in it, not on account of any active poisonous properties possessed by it, but for lack of oxygen. In the air it serves the useful purpose of diluting the oxygen. If the air consisted only of oxygen, all processes of combustion would certainly be much more active than they now are. What the effect on animals of the continued breathing of oxygen would be, it is impossible to say. The atomic weight of nitrogen is 14. Its specific gravity is 0.97. A litre of nitrogen weighs 1.2507 gram. Under a pressure of 35 atmospheres and below  $-146^\circ$  nitrogen is liquefied. It boils at  $-194^\circ$  under the ordinary atmos-

pheric pressure. Oxygen boils at  $-181^{\circ}$ , or  $13^{\circ}$  higher. Nitrogen can also be obtained in crystallized form.

**Other Constituents of the Air.**—Besides nitrogen and oxygen the air contains other substances, some of which are of great importance.

#### WATER-VAPOR IN THE AIR.

*Experiment 64.*—On a watch-glass expose a few pieces of calcium chloride to the air. What change takes place, and how is this explained? See Experiment 42, page 60. (What is a salt called which has the power to take up water from the air and dissolve in the water?)

#### CARBON DIOXIDE IN THE AIR.

*Experiment 65.*—Lime-water is made by putting a few pieces of quicklime in a bottle and pouring water upon it. The mixture is well shaken and filtered. The liquid thus obtained is lime-water, which is a solution of calcium hydroxide,  $\text{Ca}(\text{OH})_2$ , in water. Baryta-water is a solution of a similar compound of the metal barium. Expose some clear lime-water or baryta-water to the air and note the changes.

When these solutions are exposed to nitrogen or oxygen, or to an artificially prepared mixture of the two gases, no change takes place. Further, if air is first passed through a solution of caustic soda it no longer has the power to cause the formation of a crust on lime-water or baryta-water.

#### REMOVAL OF CARBON DIOXIDE FROM THE AIR.

*Experiment 66.*—Arrange an apparatus as shown in Fig. 30. The wash-cylinders *A* and *B* are half filled with a solution of caustic soda. The bottle *C* is filled with water. The tube *D* reaches to the bottom of the bottle. Being filled with water and provided with a pinch-cock, it acts as a siphon. By opening

the pinch-cock the water is caused to flow slowly out of the bottle. As it flows out, air will be drawn in through the caustic-soda solution in the wash-cylinders. When a quarter of the water in the bottle is drawn off, refill the bottle and draw off the water completely. The reason for this procedure is that the air first drawn into the bottle contains some carbon dioxide because it was not drawn through the solution of caustic soda. Now remove the stopper from the bottle, pour in 20 to 30 cc. lime-water and cork the bottle. Is there any difference between the action of this air and ordinary air? What difference?

#### REMOVAL OF WATER-VAPOR FROM THE AIR.

*Experiment 67.*—Arrange an apparatus as shown in Fig. 31 The bottle *A* contains air; *B* contains concentrated sulphuric acid; *C* is carefully dried and contains a few pieces of granulated calcium chloride and air. Pour water through the funnel-tube into *A*; the air in it will be forced through *B* and into *C*. But in

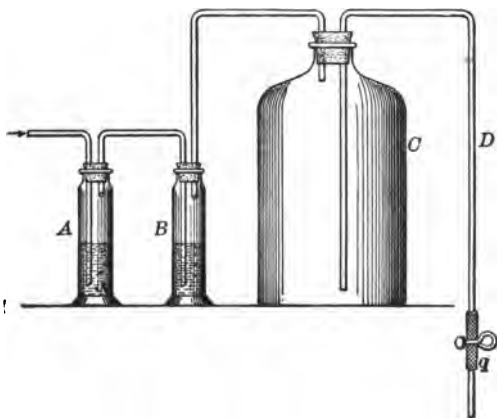


FIG. 30.

passing through *B* the moisture contained in it will be removed and the air which enters *C* will be dry. This operation may

be repeated as many times as may seem desirable. The calcium chloride in *C* will not grow moist.

**Constituents of the Air.**—The preceding experiments show that water, in the form of vapor, and carbon dioxide, which is a colorless gas, are present in the air in addition to nitrogen and oxygen. Wherever the air is examined these two substances are found to be present. Indeed, it is evident that they must be present. Evaporation is taking place everywhere, even at low temperatures, and the vapor thus formed is carried to all parts of the earth by the winds. Whenever ordinary combustible substances burn in the air, carbon dioxide is formed; and, further, the process of respiration of animals also gives rise to the formation of carbon dioxide, which is given off from the lungs.

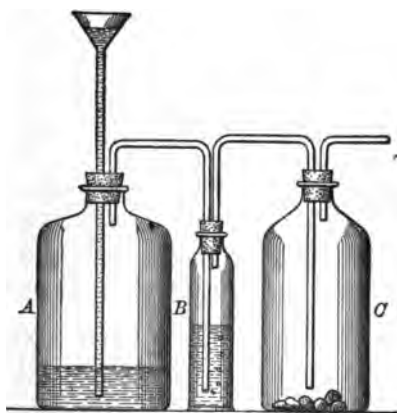


FIG. 31.

**Quantity of Water-vapor in the Air.**—The quantity of water-vapor present in the air varies between comparatively wide limits. At any given temperature the air cannot

hold more than a certain quantity. When it contains this quantity it is said to be *saturated*. If air that is saturated with water-vapor is cooled the vapor partly condenses to form water. When ice-water is put in a vessel, the air which immediately surrounds the vessel is cooled below the point of saturation, and water is deposited on the vessel. On a warm cloudy day more water is deposited on a cold object than on a clear cool day. The water-vapor present in the air has an important effect on man. Inhabitants of countries with moist climates have characteristics not generally met with in those who live in dry climates. The difference between the effect of moist and that of dry air on an individual is well known.

When air charged with water-vapor comes in contact with cooler air, the vapor condenses and falls as rain.

The quantity of water-vapor in a given volume of air can be determined by drawing the air through a weighed tube containing calcium chloride. The increase in weight will give the quantity of water in the air drawn through the tube.

**Quantity of Carbon Dioxide in the Air.**—The quantity of carbon dioxide in the air is only about 3 parts in 10,000 parts. It varies slightly according to the locality and the season. It is essential to the growth of plants.

**Argon.**—After all the carbon dioxide, water-vapor, and oxygen have been removed from the air, nitrogen remains as by far the most important constituent. But at least four other gases are mixed with it in small quantities. The principal one of these is argon. This is obtained:

1. By passing nitrogen, obtained as above, over heated magnesium which combines with it and leaves the argon;  
or



2. By adding oxygen to air contained in a vessel inverted over a solution of sodium hydroxide and provided with wires so arranged that electric sparks can be passed between their ends inside the vessel; and passing sparks for a long time through the mixture. The oxygen and nitrogen combine and the product dissolves in the solution of sodium hydroxide. After all the nitrogen has thus been removed argon remains behind.

Argon is an extremely inactive substance. No compounds of it have yet been obtained. It is present in the air to the extent of about 1 per cent of the nitrogen.

**Liquid Air.**—By subjecting air to high pressure and then letting it escape through a needle-valve it is cooled to a very low temperature. If this cold air is allowed to play upon the vessel containing the compressed air the latter is partly liquefied. Machines of this character and various others have been constructed by which air can be liquefied in any desired quantity. Liquid air evaporates very slowly if it is transported in an open vessel surrounded by a non-conductor of heat. The vessels made for this purpose are called Dewar bulbs; the Dewar bulb consists of two flasks one within the other; by fusing the outer and inner flask together at the top and pumping out the air a vacuum is obtained in the space between the flasks. The so-called "Thermos bottles" for keeping hot beverages hot, or cold beverages cold, are made in the same way.

**Oxygen Prepared from Liquid Air.**—When liquid air is allowed to stand under the ordinary pressure of the atmosphere the nitrogen boils off together with some of the oxygen,

and after a time nearly pure liquid oxygen is left. This furnishes a method of obtaining oxygen from the air.

**Other Gases in the Air.**—Besides the gases mentioned above very small quantities of three other gases have also been found in the air. These are called *krypton*, *neon*, and *xenon*. Little more is known about them than that they occur in the air.

**Summary.**—The air consists mainly of two gases one of which is oxygen.

The oxygen may be removed by means of phosphorus. Nitrogen is left.

Nitrogen does not support combustion. The air is a mixture of nitrogen and oxygen and not a chemical compound. Nitrogen is found in combination in many substances in nature.

Besides oxygen and nitrogen the air contains water-vapor, carbon dioxide, a very little argon, and other substances in very small quantities.

Air can be liquefied.

Oxygen can be obtained from liquid air.

## CHAPTER X.

### COMPOUNDS OF NITROGEN WITH HYDROGEN AND OXYGEN.

**General Conditions which Give Rise to the Formation of the Simpler Compounds of Nitrogen.**—It has been shown that nitrogen is an inactive element. It is nevertheless an easy matter to get compounds of nitrogen with many other elements, and among these compounds, some of those which it forms with hydrogen and oxygen are very important.

Whenever a compound containing carbon, hydrogen, and nitrogen is heated in a closed vessel, so that the air does not have access to it and it cannot burn, the nitrogen passes out of the compound, not as nitrogen, but to some extent in combination with hydrogen, in the form of the compound called *ammonia*. Nearly all animal substances contain carbon, hydrogen, oxygen, and nitrogen, and many of them give off ammonia when heated. Some animal substances give off ammonia when they undergo decomposition in the air. The coal which is used for making illuminating-gas contains some hydrogen and nitrogen in chemical combination, and when the coal is heated ammonia is given off.

Compounds of metals with nitrogen, called nitrides, give ammonia when acted upon by steam.

When animal substances undergo decomposition in the

presence of a base where the temperature is comparatively high, the nitrogen combines with oxygen and the metal of the base, forming either a nitrite or a nitrate, that is to say, either a salt of nitrous acid,  $\text{HNO}_2$ , or of nitric acid,  $\text{HNO}_3$ . In some countries where the conditions are favorable to the process, immense quantities of nitrates are found, chiefly potassium nitrate, or saltpetre,  $\text{KNO}_3$  (which see), and sodium nitrate, or Chili saltpetre,  $\text{NaNO}_3$  (which see). The change of the nitrogen of animal substances to the form of nitrates is caused by minute living organisms. How they effect the change is not known. From the salts of nitric acid which are found in nature, nitric acid itself can easily be prepared.

When electric sparks are passed through a mixture of nitrogen and oxygen the two gases slowly combine. If water and a base are present a nitrite and a nitrate will be formed.

Nearly all the compounds of nitrogen with which we shall have to deal are made either from ammonia or from nitric acid.

**Ammonia,  $\text{NH}_3$ .**—The conditions under which ammonia is formed have been mentioned. The chief source in some countries is the "ammonia-water" of the gas-works. This is the water through which the gas has been passed for the purpose of removing the ammonia, which passes into solution. By adding hydrochloric acid to this liquid, *ammonium chloride*, which is a compound of the acid with ammonia, is formed. This is the well-known substance *sal ammoniac*. It appears that this name had its origin in the fact that common salt was formerly called *sal armeniacum*. and

that afterward, through a misunderstanding, ammonium chloride came to be known by the same name which underwent change to the form *sal ammoniacum*, or *sal ammoniac*. Large quantities of ammonia are made by distilling waste animal products.

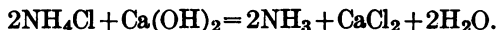
As ammonium chloride, or *sal ammoniac*, is the most common compound containing ammonia, it is used in the laboratory for making ammonia. For this purpose it is only necessary to treat the salt with an alkali.

#### AMMONIA.

*Experiment 68.*—To a little ammonium chloride on a watch-glass add a few drops of a strong solution of caustic soda, and notice the odor of the gas given off. Do the same thing with caustic potash. Mix small quantities of ammonium chloride and lime in a mortar and notice the odor. Has the ammonium chloride itself this odor?

**Preparation of Ammonia.**—Ammonia is best prepared by mixing slaked lime and ammonium chloride.

In addition to the ammonia, which is given off in the form of gas, calcium chloride,  $\text{CaCl}_2$ , and water are formed in this reaction. It is represented thus:



This curious reaction will be more fully discussed after ammonia has been studied.

#### PREPARATION OF AMMONIA.

*Experiment 69.*—Arrange an apparatus as shown in Fig. 27, page 122; omitting, however, the funnel-tube; a cork with one opening will therefore suffice. Weigh 100 grams powdered quicklime into the flask and 50 grams ammonium chloride and mix by

shaking. Add 50 cc. warm water and push the stopper into place. A rapid evolution of ammonia will soon commence and it will not be necessary to heat the flask. After the air is driven out, the gas will be completely absorbed by the water in the first Woulff flask. Disconnect the delivery-tube from the Woulff flasks, and connect with another tube bent upward.

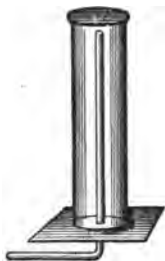


Fig. 32.

Collect some of the escaping gas by displacement of air, *placing the vessel with the mouth downward*, as the gas is much lighter than air. The arrangement is shown in Fig. 32. The vessel in which the gas is collected should be dry, as water absorbs ammonia very readily. Hence, also, it cannot be collected over water. In the gas collected introduce a burning stick or taper. Ammonia does not burn in air, nor does it support combustion. In working with the gas great care must be taken to avoid inhaling it in any

quantity. After a vessel has been filled, connect the delivery-tube again with the Woulff flasks, and pass the gas over the water as long as it is given off.

**Properties of Ammonia.**—From these experiments it is seen that ammonia is a colorless, transparent gas. It has a very penetrating characteristic odor. In concentrated form it causes suffocation. Its specific gravity is 0.59; that is to say, it is but little more than half as heavy as air. It can easily be reduced to the liquid form by pressure and cold. When the pressure is removed from the liquefied ammonia, it passes back to the form of gas. In so doing it absorbs heat.

Ammonia does not burn in the air, but does burn in oxygen. It is absorbed by water in very large quantity. One volume of water at the ordinary temperature dissolves about 600 volumes of ammonia-gas, and at 0° about 1000 volumes.

[PROBLEM.—A litre of air at  $0^{\circ}$  weighing 1.293 grams, and the specific gravity of ammonia-gas being 0.59, how much would a litre of water increase in weight by being saturated with ammonia at  $0^{\circ}$ ?]

The solution of ammonia in water is generally called ammonia in the laboratory. It was formerly called "spirits of hartshorn." The solution has the odor of the gas. It loses all its gas when boiled for some time. The solution shows a strong alkaline reaction and has the power to neutralize acids.

#### COMBINATION OF HYDROCHLORIC ACID AND AMMONIA.

*Experiment 70.*—(T) Fill a cylinder with ammonia-gas, and another of the same size with hydrochloric-acid gas. Bring them together with their mouths covered. Quickly withdraw the covers. A dense white cloud will appear in and about the cylinders. Most of this will soon settle on the walls of the vessels as a light white solid. It is ammonium chloride. Thus, from two colorless gases a solid substance is obtained by an act of chemical combination. Heat is evolved in the act of combination.

*Experiment 71.*—Put 100 cc. of a *dilute* solution of ammonia in an evaporating-dish. Try its effect on red litmus paper. Slowly add dilute hydrochloric acid until the alkaline reaction is destroyed and the solution is neutral. Evaporate to dryness on a water-bath. Compare the substance thus obtained with sal ammoniac or ammonium chloride. Taste them. Heat them on a piece of platinum-foil. Treat them with caustic soda or caustic potash. Treat with a little concentrated sulphuric acid in dry test-tubes. Do they appear to be identical?—The product is ammonium chloride,  $\text{NH}_4\text{Cl}$ . Similarly sulphuric acid and ammonia yield ammonium sulphate; nitric acid and ammonia yield ammonium nitrate, etc.

**Carré's Ice-machine.**—The cold that is produced by allowing liquefied ammonia to pass into the form of gas is utilized

for the manufacture of ice and for cooling purposes in general. The principle of the machine is easily understood. A saturated solution of ammonia in water or in an aqueous solution of calcium chloride is gradually warmed. The ammonia-gas is driven out of the solution and is made to pass into a series of pipes surrounded by brine. The gas is prevented from escaping from the pipes and is liquefied when the pressure becomes high enough. On now removing the pressure by opening the pipes the temperature of the brine is lowered and ice may be made by placing closed cans of water in it, or the brine may be circulated through pipes in rooms which it is desired to cool. The ammonia-gas that passes off may again be liquefied and again used for cooling.

**Salts Formed by Ammonia.**—It has been shown that the alkalies are strong bases, and that bases are compounds of metals with hydrogen and oxygen. Certainly those substances which show an alkaline reaction, that is to say, react with litmus and other colors the same as the alkalies do, are compounds of metals with hydrogen and oxygen, and the alkaline reaction and basic properties are believed to be due to the hydroxyl,  $\text{OH}$ . Now in the solution of ammonia in water there is a substance which shows an alkaline reaction and acts in nearly all respects much like a solution of sodium hydroxide or potassium hydroxide. The salts which ammonia forms with acids are similar to the salts of sodium and potassium. What is the substance that has the alkaline reaction? and what are the salts that are formed by the action of acids on ammonia?

In the first place, it has been found that when an acid acts



on ammonia the two combine directly without the formation of anything but the salt. Thus ammonia and hydrochloric acid form ammonium chloride:



Ammonia and nitric acid form ammonium nitrate:

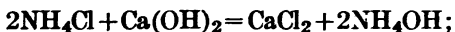


**Ammonium Theory.**—On comparing the formulas of ammonium salts with those of potassium and sodium salts it will be seen that, while in the potassium and sodium salts the metals potassium and sodium take the place of the hydrogen of the acids, in the ammonium salts the place of the hydrogen of the acid is taken by a group of elements having the formula  $\text{NH}_4$ . It has been suggested, and the idea has been generally accepted, that when ammonia-gas dissolves in water the ions  $\text{NH}_4$  and  $\text{OH}$  of an unstable compound of the formula  $\text{NH}_4\text{OH}$  are formed thus:

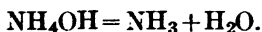


In this hydroxide, as in the salts of ammonia, the group or ion  $\text{NH}_4$  appears to play the part of a metal ion. The group  $\text{NH}_4$  has never been isolated. As it appears to be this which plays the part of a metal in the solution as well as in the salts, the name *ammonium* has been given to it, the ending *ium* being that which is usually given to signify metallic character. We speak, then, of *ammonium salts*, just as we speak of potassium or sodium or calcium salts. In the ammonium salts the hypothetical compound metal ammonium,  $\text{NH}_4$ , is assumed to be present. If, however, we attempt to set it free or to set its hydroxide free, we

get ammonia. On treating ammonium chloride with lime, if any action takes place at all, we should expect it to be that represented by the equation.



that is to say, we should expect the calcium and ammonium to exchange places. Perhaps this is the action that takes place at first. But the compound  $\text{NH}_4\text{OH}$ , or ammonium hydroxide, if formed at all, breaks up at once into ammonia and water, thus:



So, too, if ammonium hydroxide,  $\text{NH}_4\text{OH}$ , and its ions  $\text{NH}_4$  and  $\text{OH}$ , are present in the solution of ammonia in water, a rearrangement takes place very readily and ammonia and water are formed under the influence of gentle heat, and ammonia-gas is given off.

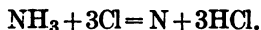
**Composition of Ammonia by Weight.**—By oxidation it is possible to convert the hydrogen of ammonia into water and leave the nitrogen in the free state. As water and nitrogen are the only products formed, and the quantity of oxygen used up in the oxidation is equal to the quantity of oxygen found in the water formed, it follows that nitrogen and hydrogen are the only elements contained in ammonia.

When electric sparks are passed for some time through a mixture of nitrogen and hydrogen, some ammonia is formed. Conversely, when electric sparks are passed for a time through ammonia, nitrogen and hydrogen are obtained.

If, in the oxidation of a known quantity of ammonia the water formed and the nitrogen left uncombined are accurately determined, it will be found that in ammonia

the elements are combined in the proportion of *fourteen parts by weight of nitrogen to three parts by weight of hydrogen*. This fact is expressed by the formula  $\text{NH}_3$ ; 14 being the atomic weight of nitrogen.

**Composition of Ammonia by Volume.**—The proportion by volume in which the two elements combine may be determined by the following method.\* When ammonia is treated with chlorine it is decomposed, the chlorine combining with hydrogen, and the nitrogen being left uncombined. The reaction is represented thus:



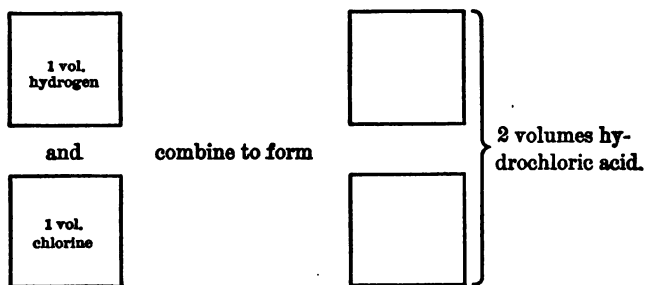
Hydrogen and chlorine unite in equal volumes, as has already been seen. Now, if a solution of ammonia is added to a measured volume of chlorine until the chlorine is all used up, the volume of hydrogen which is extracted from ammonia is equal to the volume of chlorine used. The nitrogen left over was combined with the hydrogen whose volume has already been determined. It would be found that the volume of nitrogen is to that of the hydrogen with which it was combined as 1 to 3; or *in ammonia 1 volume of nitrogen is combined with 3 volumes of hydrogen*.

When a given volume of ammonia is decomposed into nitrogen and hydrogen, the mixture occupies just twice the volume that the ammonia did; or, if nitrogen and hydrogen in the proper proportions to form ammonia are caused to combine, the ammonia formed occupies one half the volume occupied by the mixture of the two gases.

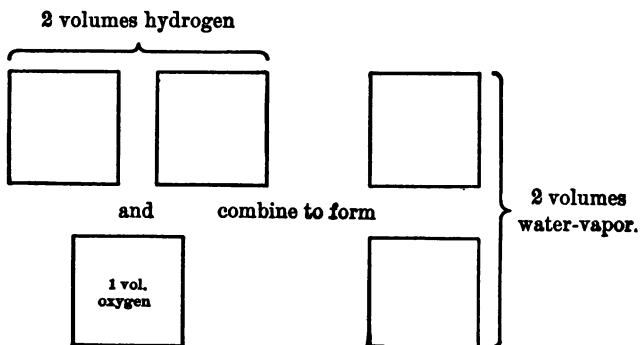
\* This experiment requires so many precautions and is so dangerous unless the precautions are taken that teachers are not advised to perform it, as a rule.

**Relations between the Volumes of Combining Gases.—**

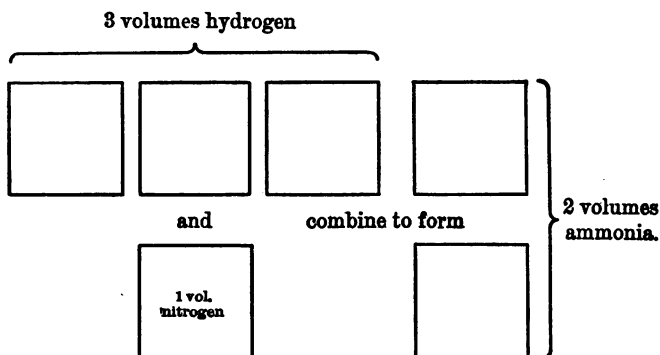
In studying the volume-relations of hydrogen, chlorine, and hydrochloric acid with reference to one another, we found that when hydrogen and chlorine combine one volume of the one combines with one volume of the other, and two volumes of the product are formed. These facts may be represented graphically thus:



When hydrogen and oxygen combine, two volumes of hydrogen combine with one volume of oxygen; and the three volumes of gas thus combined form two volumes of water-vapor:



Finally, it has just been shown that one volume of nitrogen combines with three volumes of hydrogen to form two volumes of ammonia:



**Gay Lussac's Law of Volumes.**—*A careful study of the volumes of combining gases has shown that these volumes always bear a simple relation to one another and to the volumes of the products formed.* The three cases above presented show the more common relations met with among the elements.

**Condensation or Contraction.**—It is clear that the three elements chlorine, oxygen, and nitrogen influence hydrogen differently. One volume of chlorine can hold in combination but one volume of hydrogen. One volume of oxygen can hold in combination two volumes of hydrogen, and at the same time it causes a condensation of volume from three volumes of gas to two. One volume of nitrogen can hold in combination three volumes of hydrogen, and at the same time it causes a condensation of four volumes of gas to two. The explanation of this contraction of volume will be given later.

**Relation between the Specific Gravities of Gases and their Atomic Weights.**—Attention has already been called to the fact that the weights of equal volumes of hydrogen, chlorine, and oxygen stand in the same relation to one another as the combining weights. Nitrogen is no exception to this rule. The specific gravity of nitrogen is 0.967. One litre of nitrogen weighs 1.2507 grams. The specific gravity of hydrogen is 0.0696; and the weight of a litre of hydrogen is 0.08995. But  $0.0696:0.967::1:14$  and, of course,  $0.08995:1.2507::1:14$ . The accepted combining weight of nitrogen is 14.

These remarkable facts may be represented graphically thus:



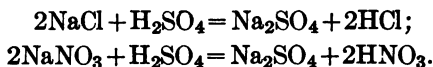
These figures bear to one another very nearly the relations expressed by the figures 1, 35.4, 16, and 14. But these last figures very nearly express the atomic weights of the elements. It appears, therefore, that *the atomic weights of some of the gaseous elements bear to one another the same relations as the weights of equal volumes of the gases.*

Observations of this kind, together with other observations on the conduct of gases, have led to a very important conception in regard to the nature of gases and the constitution of matter. This will be treated of farther on. For the present it will be best to keep to the facts, so that before taking up speculations in regard to the hidden causes of the phenomena observed we may gain a solid

foundation for these speculations. It should also be borne in mind that the object of speculation is not to devise theories for their own sake, but to help us to understand the facts, and to lead to the discovery of other facts.

**Nitric Acid,  $\text{HNO}_3$ .**—To effect the direct union of nitrogen with oxygen and hydrogen is not easier than to effect the direct union of nitrogen with hydrogen to form ammonia. Nevertheless, the silent and continuous action of minute organisms in the soil is always tending to transform the waste-products of animal life into compounds closely allied to nitric acid. The process of *nitrification* has already been referred to. It is plainly an oxidizing process. In general, by oxidation the nitrogen of animal substances is converted into nitric acid, while by reduction it is converted into ammonia.

**Preparation of Nitric Acid.**—In preparing nitric acid a nitrate is always used as the starting-point, and in this the hydrogen is substituted for the metal. This is done in the same way that hydrogen is substituted for the metal sodium in sodium chloride in the preparation of hydrochloric acid,—*viz.*, by treating the salt with some acid:



In these cases the acids obtained are volatile under the conditions of the experiment. *Acids that are not volatile under the conditions of the experiment decompose the salts of those that are.* At a sufficiently high temperature sulphuric acid is volatile, and an acid that is not volatile at such a temperature will set sulphuric acid free.

## PREPARATION OF NITRIC ACID.

**Experiment 72.**—Arrange an apparatus as shown in Fig. 33. In the retort put 40 grams sodium nitrate (Chili saltpetre) and 20 grams concentrated sulphuric acid. On heating *with a small flame*, nitric acid will distil over, and be condensed in the receiver. After the acid is all distilled off, remove the contents of the retort. Recrystallize the substance from water, and compare it with the sodium sulphate obtained in the preparation of hydrochloric acid.

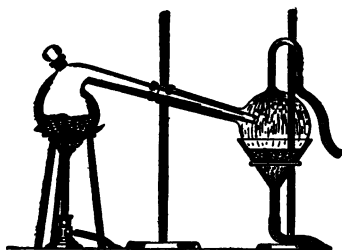


FIG. 33.

(See Experiment 57, page 121.) In the latter stages of the operation the vessels become filled with a reddish-brown gas. The acid which is collected has a somewhat yellowish color.

On the large scale the acid is made by bringing Chili saltpetre and concentrated sulphuric acid together in cast-iron cylinders or retorts.

**Nitric Acid and Nitrates from Atmospheric Nitrogen.**—The world's supply of nitric acid and nitrates is drawn at present mostly from the Chili saltpetre deposits. According to recent official statistics the deposits will be exhausted in twenty years. Although still more recently (1907) the discovery of new deposits of large extent is



announced, this will only postpone the time of exhaustion, as 1,400,000 tons was consumed—largely as fertilizer—in 1905, and the demand is increasing rapidly.

Of many attempts to obtain oxides of nitrogen directly and nitric acid indirectly from the air by the action of electric sparks or the electric arc, the one which is of greatest promise commercially is that of Birkeland and Eyde now in use on a large scale in Norway.

The process utilizes the action of the magnetic field on the arc. With a powerful alternating current forming arcs, and powerful electro-magnets, glowing electric discs are produced built up of arcs deflected from the terminals by the magnetic field. In practice these discs are six feet in diameter, and have a temperature of over 2000°. The discs are enclosed in a circular furnace (like a wheel set on edge) and a rapid current of air passes across its diameter. The gas leaving the furnace is a mixture of nitric oxide, nitrogen and unchanged air. This passes into granite towers filled with porous material over which water drips, where the following reactions occur:



When all of the nitric oxide is changed into acid, the latter is treated with lime and gives calcium nitrate. This is now the market product. It is said to be a better fertilizer than Chili saltpetre.

Another commercial fertilizer made from atmospheric nitrogen is calcium cyanamide (which see).

**Pure nitric acid** is a colorless liquid. It gives off colorless fumes when exposed to the air. When boiled it under-

goes slight decomposition into oxygen, water, and compounds of nitrogen and oxygen. One of these compounds is colored, and it is this that is noticed in the above experiment, and whenever strong nitric acid is boiled. Nitric acid undergoes a similar decomposition when exposed to the action of the direct rays of the sun. In consequence of this decomposition bottles containing strong nitric acid always contain a reddish-brown gas above the liquid after standing for some time. It acts violently on a great many substances, disintegrating them. It causes bad wounds in contact with the flesh; eats through clothing; burns wood; dissolves metals; and is altogether one of the most active of chemical substances. In working with the concentrated acid it is necessary to exercise the greatest care.

**Commercial nitric acid** contains only about 68 per cent of the chemical compound  $\text{HNO}_3$ . The rest is mostly water, though there are several impurities present in small quantity. In order to get concentrated pure acid from this it must be distilled after the addition of some concentrated sulphuric acid.

#### CONCENTRATED NITRIC ACID.

*Experiment 73.*—(T) Mix 200 grams concentrated sulphuric acid and 100 grams ordinary concentrated nitric acid. Pour the sulphuric acid slowly into the nitric acid. Distil the mixture very slowly from a retort arranged as in Experiment 72, taking care to keep the neck of the retort cool by placing filter-paper moistened with cold water on it. Use the acid thus obtained for the purpose of studying the properties of pure nitric acid. N.B. *The substance is dangerous, and these experiments require great caution!*

**Nitric Acid an Oxidizing Agent.**—In consequence of the ease with which nitric acid decomposes, giving up oxygen,

it is an excellent oxidizing agent, and is much used in the laboratory in this capacity. The following experiments illustrate this action:

NITRIC ACID AN OXIDIZING AGENT.

*Experiment 74.—(T) See Note at the end of Experiment 73.—The gases given off from the tube are offensive and poisonous. Hence this as well as all other experiments with nitric acid should be carried on under a hood in which there is a good draught. Pour some fuming nitric acid into a wide test-tube, so that it is*

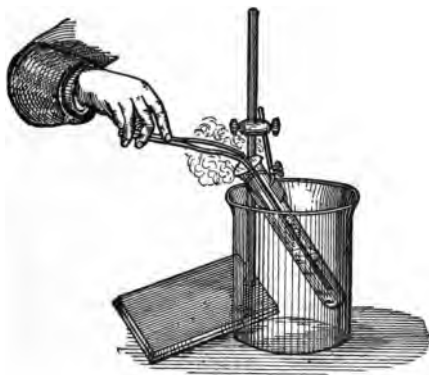


FIG. 34.

about one fourth filled. Heat the end of a stick of charcoal of proper size, and, holding the other end with a forceps, introduce the heated end into the acid.—It will continue to burn with a bright light, even though it is placed below the surface of the liquid. The action is oxidation. The charcoal in this case finds the oxygen in the acid, and not in the air. Great care must be taken in performing this experiment. The charcoal should not come in contact with the sides of the test-tube. A large beaker-glass should be placed beneath the test-tube, so that, in case it should break, the acid will be caught and prevented from doing harm. The arrangement of the apparatus is shown in Fig. 34.

*Experiment 75.*—(T) Boil a little fuming nitric acid in a test-tube in the upper part of which some woolen yarn has been introduced in the form of a stopper. The woolen yarn will take fire and burn, leaving a white residue. Hold the test-tube with a forceps over a vessel to catch the contents should the tube break.

*Experiment 76.*—(T) In a small flask put a few pieces of granulated tin. Pour on this just enough ordinary concentrated nitric acid to cover it. Heat gently over a small flame. Soon action will take place. Colored gases will be evolved, the tin will disappear, and in its place will be found a white powder. This consists mostly of tin and oxygen. (See Experiment 15, page 16.)

**Action of Nitric Acid on Metals.**—Like other acids, nitric acid forms salts with the metals. These can be made by treating the metals themselves with the acid, but in this case the formation of the salt is accompanied by another kind of action which is quite characteristic of nitric acid. The acid gives up a part of its oxygen and is thus converted into compounds of oxygen and nitrogen which contain a smaller proportion of oxygen than the acid. The compound most commonly formed in this way is nitric oxide, NO. It appears probable that the metal first abstracts oxygen from the acid, and that the oxide thus formed then dissolves in a part of the acid as the nitrate. The action in the case of copper should, according to this, be represented as taking place in two stages. First, nitric oxide, water, and copper oxide are formed as represented in this equation:



Then the copper oxide forms copper nitrate with some of the acid, and this nitrate dissolves:



Nitric oxide,  $\text{NO}$ , unites with oxygen from the air, and forms nitrogen peroxide,  $\text{NO}_2$ , a colored gas, which is always seen when nitric acid acts upon metals.

#### ACTION OF NITRIC ACID ON COPPER.

*Experiment 77.*—Dissolve a few pieces of copper-foil or copper turnings in ordinary commercial nitric acid diluted with about half its volume of water. The operation should be carried on in a good-sized flask and under an efficient hood. When the copper has disappeared, pour the blue solution into an evaporating-dish, and evaporate down to crystallization. Compare the substance thus obtained with copper nitrate.—Heat a specimen of each.—Treat small specimens with sulphuric acid.—Do the two substances appear to be identical?

#### NITRATES DECOMPOSED BY HEAT.

*Experiment 78.*—Heat in dry glass tubes specimens of potassium nitrate, sodium nitrate, lead nitrate, and any other nitrates that may be available. All are decomposed, giving off oxygen, in some cases mixed with oxides of nitrogen, among which is nitrogen peroxide, which can be recognized by its color.

**General Properties of the Salts of Nitric Acid.**—All salts of nitric acid are decomposed by heat, and all are soluble in water.

#### SOLUBILITY OF NITRATES IN WATER.

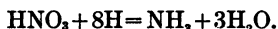
*Experiment 79.*—Try the solubility in water of specimens of the nitrates that were used in the last experiment.

**Ammonia Formed by Reduction of Nitric Acid.**—The formation of ammonia by reduction of nitric acid may be shown by the following experiment.

## REDUCTION OF NITRIC ACID TO AMMONIA.

*Experiment 80.*—In a small beaker treat a few pieces of granulated zinc with dilute sulphuric acid. What is evolved? While this gas is being evolved add *drop by drop* about 5 cc. dilute nitric acid. As soon as the nitric acid has been added filter the solution and evaporate the filtrate to dryness in a porcelain dish. Put some of the residue into a strong solution of caustic soda. What is given off? Try the action of the gas on red litmus paper. Moisten the end of a glass rod with a little hydrochloric acid and hold it in the tube. What do you observe? Explain it. Do the same with nitric acid. What are the fumes in this case?

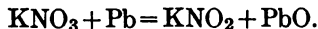
In this case the nitric acid is reduced to ammonia by the hydrogen, a reaction that is represented thus:



But the ammonia combines with the acid and forms a salt. The caustic soda is used to set the ammonia free.

**Aqua Regia.**—*Aqua regia* is made by mixing together concentrated nitric and hydrochloric acids. It received its name for the reason that it can dissolve gold, which was formerly called the king of metals. It is an excellent solvent, and is much used in the laboratory.

**Nitrous Acid,  $\text{HNO}_2$ .**—Among the reduction-products of nitric acid is nitrous acid,  $\text{HNO}_2$ . A salt of this acid is most easily prepared by reducing a nitrate. Thus, if potassium nitrate,  $\text{KNO}_3$ , is melted together with metallic lead, the lead extracts a part of the oxygen and leaves potassium nitrite,  $\text{KNO}_2$ :

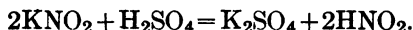


## NITROUS ACID AND NITRITES.

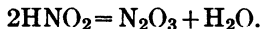
*Experiment 81.*—Heat together in a shallow iron pan 25 grams potassium nitrate and about 50 grams metallic lead. When

both are melted continue the heating and stir the substances together as thoroughly as possible until all the lead has disappeared. After the mass has cooled down, add water and heat until the mass becomes loosened from the pan. By this time the nitrite will have dissolved while the lead oxide will remain undissolved. Filter. Add a little sulphuric acid to some of the solution. What is given off? See whether a solution of potassium nitrate acts in the same way.

**Nitrous Acid breaks down into Nitrogen Trioxide and Water.**—When an acid is added to a solution of a nitrite, the salt is decomposed and *nitrogen trioxide* or *nitrous anhydride*,  $N_2O_3$ , is given off. Were the action in this case analogous to that which takes place when sulphuric acid acts upon a nitrate or upon a chloride, it would be represented thus:



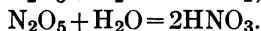
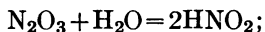
Nitrous acid would be formed. But instead of this a substance which is nitrous acid minus the elements of water is formed:



This tendency on the part of compounds containing hydrogen and oxygen to decompose with formation of water is very commonly observed. We have already had to deal with a case of the kind in ammonium hydroxide. This substance, which probably exists in solution in water, yields ammonia and water when heated. Many compounds that do not break up in this way at ordinary temperatures do so at elevated temperatures. This decomposition is to be ascribed to the strong tendency of hydrogen to combine with oxygen. In complex compounds several forces are at work to keep the constituents in equilibrium. If the

attraction of hydrogen for oxygen is much stronger than the other forces at work, the equilibrium is disturbed, and decomposition takes place.

**Anhydrides.**—A compound which, in its composition, bears to an acid the relation that nitrogen trioxide,  $N_2O_3$ , bears to nitrous acid,  $HNO_2$ , is called an *anhydride*. Thus we have *nitrous anhydride*,  $N_2O_3$ ; *nitric anhydride*,  $N_2O_5$ , etc. Nitric anhydride bears the same relation to nitric acid that nitrous anhydride bears to nitrous acid:



In more general terms, it may be said that any oxide which, when brought together with water, forms an acid by direct combination is an anhydride. Other examples of this class of compounds will be met with farther on.

**The Oxides of Nitrogen.**—Nitrogen and oxygen form five compounds with each other, of which all but one have already been mentioned. The names and formulas of the five compounds are nitrogen peroxide,  $NO_2$ ; nitric oxide,  $NO$ ; nitrous oxide,  $N_2O$ ; nitrous anhydride,  $N_2O_3$ ; and nitric anhydride,  $N_2O_5$ . If the formulas of these compounds are arranged in a series, beginning with that one which contains the smallest proportion of oxygen, it will be seen that the series affords a striking illustration of the facts from which the law of multiple proportions is deduced.\* The series is:

Nitrous oxide.....	$N_2O$
Nitric oxide.....	$NO$ or $N_2O_2$
Nitrogen trioxide.....	$N_2O_3$
Nitrogen peroxide.....	$NO_2$ or $N_2O_4$
Nitric anhydride.....	$N_2O_5$

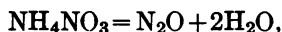


Clearly the weights of oxygen combined with 28 parts by weight of nitrogen are 16, 32, 48, 64, and 80.

[What other series of compounds have we already had to deal with that illustrates the law of multiple proportions almost equally strikingly? (See page 131.)]

Of the oxides of nitrogen, only three need be studied here, and after what has already been said they need be studied only briefly.

**Nitrous Oxide,  $N_2O$ .**—This compound is formed by reduction of nitric acid when the acid acts upon metals and the degree of concentration and the temperature are favorable. It is usually prepared by heating ammonium nitrate,  $NH_4NO_3$ . The decomposition takes place as represented thus:



the products being nitrous oxide and water. In this reaction the tendency of hydrogen and oxygen to combine at elevated temperatures is shown. At ordinary temperatures this tendency is not strong enough to cause a disturbance of the equilibrium of the constituents of the compound. As the temperature is elevated it becomes stronger and stronger, until finally the decomposition above represented takes place and the elements combine.

#### NITROUS OXIDE.

*Experiment 82.*—In a retort, heat 10 to 15 grams crystallized ammonium nitrate until it has the appearance of boiling. *Do not heat higher than is necessary to secure a regular evolution of gas.* Connect a wide rubber tube directly with the neck of the retort and collect the evolved gas over water, as in the case of oxygen. It supports combustion almost as well as pure oxygen,

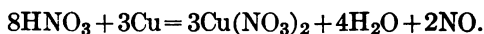
Try experiments with wood, a candle, and a piece of phosphorus in a deflagrating-spoon.

**Properties.**—The gas is colorless and transparent. It has a slightly sweetish taste. It is somewhat soluble in water, so that when collected over water there is always considerable loss. When inhaled it causes a kind of intoxication, which is apt to show itself in the form of hysterical laughing, hence the name *laughing-gas*. Inhaled in larger quantity it causes unconsciousness and insensibility to pain. It is therefore used to prevent pain in minor surgical operations, as, for example, in pulling teeth. It supports combustion almost as well as pure oxygen.

Nitrous oxide is easily converted into a liquid by cold and pressure. In this form it can now be bought contained in strong iron cylinders. On opening the stop-cock of the cylinder the substance escapes in gaseous form.

**Nitric Oxide, NO.**—This gas is formed when nitric acid acts upon some metals, as copper. The action is believed to involve two changes, as described on page 182.

The two equations representing the action may be combined in one, thus:



#### NITRIC OXIDE.

*Experiment 83.*—Arrange an apparatus as shown in Fig. 35. In the flask put a few pieces of copper-foil. Cover this with water. Now add slowly, waiting each time for the action to begin, *ordinary* concentrated nitric acid. When enough nitric acid has been added, gas will be evolved. If too much acid is added, it not infrequently happens that the evolution of gas takes place too rapidly, so that the liquid is forced out of the

flask through the funnel-tube. This can be avoided by not being in a hurry. At first the vessel becomes filled with a reddish-brown gas, but soon the gas evolved becomes colorless. Collect over water two or three vessels full. The gas collected is principally nitric oxide, NO, though it is frequently mixed with a considerable quantity of nitrous oxide.

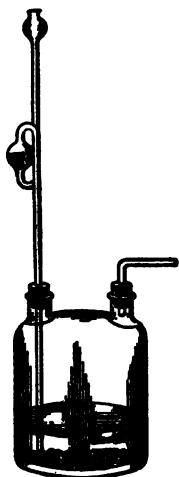
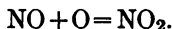


FIG. 35.

*Experiment 84.*—Perform the experiment with nitric oxide where there is a good draught. Turn one of the vessels containing colorless nitric oxide with the mouth upward and uncover it. A colored gas is at once seen, presenting a very striking appearance. Do not inhale the gas. Put a burning splinter of wood in one of the vessels containing nitric oxide. Into another put a deflagrating-spoon containing burning sulphur. Burning phosphorus will continue to burn in the gas.

**Properties of Nitric Oxide.**—Nitric oxide is a colorless, transparent gas. Its most remarkable property is its power to combine directly with oxygen when the two are brought together. The act of combination is not accompanied by the appearance of light, though heat is evolved. The reaction is represented by the equation



The product is nitrogen peroxide, and this at ordinary temperatures is a reddish-brown gas.

Nitric oxide does not burn. Most burning substances are extinguished when introduced into it, though a few when heated in it to a high temperature extract all or a part of the oxygen. When the fact is borne in mind that

nitrous oxide,  $N_2O$ , supports combustion almost as well as oxygen, it appears strange that another compound of nitrogen and oxygen, containing twice as much oxygen relatively to the same quantity of nitrogen, should not generally support combustion. This is explained by the relative stability of the two compounds. In the case of nitrous oxide, the oxygen is not firmly held in combination. Hence, when a substance that readily combines with oxygen is brought in contact with it the oxide is decomposed. On the other hand, in nitric oxide the arrangement of the constituents is a more stable one. The oxygen, although present in larger quantity than in nitrous oxide, is held in combination more firmly, and cannot easily be extracted. The gas does not ordinarily support combustion.

**Nitrogen Peroxide,  $NO_2$ .**—This gas is made by direct combination of nitric oxide with oxygen, as seen in the last experiment. It has a disagreeable smell and is poisonous. It gives up a part of its oxygen quite easily, and is hence useful as an oxidizing agent.

**Use of the Oxides of Nitrogen in the Manufacture of Sulphuric Acid.**—The higher oxides of nitrogen, especially the trioxide,  $N_2O_3$ , and the peroxide,  $NO_2$ , readily give up oxygen, and are changed to nitric oxide,  $NO$ . If air is present, nitric oxide is changed back again to the higher oxides, which may again give up oxygen, again yielding nitric oxide, and so on indefinitely. It will thus be seen that these oxides of nitrogen may be made to serve the purpose of transferring oxygen from the air to other substances. Advantage is taken of these facts in the manufacture of sulphuric acid.

**Summary.**—The simpler nitrogen compounds are made either from ammonia or from nitric acid. Ammonia is formed in nature by the decomposition of animal substances. It is also formed by heating substances which contain carbon, hydrogen, and nitrogen.

Nitric acid is formed in nature as the potassium or sodium salt, by the action of certain organisms on substances containing nitrogen.

Ammonia is prepared from an ammonium salt by treating it with a strong base. Ammonium chloride and lime are commonly used.

With acids ammonia forms salts which are known as ammonium salts, and in which the group  $\text{NH}_4$  is believed to play the part of a metal. This hypothetical metal is called *ammonium*.

Ammonia consists of 14 parts by weight of nitrogen to 3 of hydrogen. The gases are combined in the proportion of 1 volume of nitrogen to 3 volumes of hydrogen. The 4 volumes thus combined condense to 2 volumes of ammonia.

There is always a simple relation between the volumes of combining gases and the volume of the compound formed if it is a gas.

A comparison of the specific gravities of the gaseous elements thus far studied shows that these bear to one another the same relation as the atomic weights.

Nitric acid is prepared from a nitrate by treating it with sulphuric acid. It is comparatively unstable, giving up oxygen easily. With metals it yields salts, but the action involves the reduction of a part of the acid, and leads to the formation of various products, among which may be nitrous oxide,  $\text{N}_2\text{O}$ ; nitric oxide,  $\text{NO}$ ; nitrous anhydride,

$\text{N}_2\text{O}_3$ ; and nitrogen peroxide,  $\text{NO}_2$ . Under some circumstances, the action may even go far enough to form ammonia.

Nitrous acid itself is unstable, breaking up into the anhydride,  $\text{N}_2\text{O}_3$ , and water.

Anhydrides are substances which, when brought together with water, combine with it to form acids.

Though nitrous oxide is formed by reduction of nitric acid, it is best prepared in pure condition by heating ammonium nitrate. It is a good supporter of combustion.

Nitric oxide is made by reduction of nitric acid by means of copper. It combines directly with oxygen, forming the strongly colored and disagreeable-smelling nitrogen peroxide.

Nitrogen peroxide gives up a part of its oxygen easily and is hence a good oxidizing agent. It is thus reduced to nitric oxide, which in the air takes up oxygen.



## CHAPTER XI.

### AVOGADRO'S HYPOTHESIS. — MOLECULAR WEIGHTS. — MOLECULAR FORMULAS.—VALENCE.

**Avogadro's Hypothesis.**—Early in the last century the Italian physicist and chemist, Avogadro, was led to the conclusion that *equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules*, the molecule of a substance being the smallest particle of that substance as it exists in the free state or uncombined (see page 93). This is known as Avogadro's hypothesis. It has since been tested in many ways, and has always asserted itself as correct. At the present time it forms one of the most important foundations of thought in regard to chemical phenomena.

**Molecules and Molecular Weights.**—According to Avogadro's hypothesis the weights of the molecules of substances bear to each other the same relation as the weights of equal volumes of these substances in the form of gas or vapor. The weights of equal volumes of gases or vapors can easily be determined. It has been found that the following figures express the relative weights of equal volumes of the gases or vapors named. The weights are compared to that of

hydrogen for the reason that it is the lightest of all substances known:

Substance	Relative Weights of Equal Volumes.
Hydrogen. . . . .	1
Marsh-gas. . . . .	8
Ammonia. . . . .	8.5
Water-vapor. . . . .	9
Hydrocyanic acid. . . . .	13.5
Carbon monoxide. . . . .	14
Nitric oxide. . . . .	15
Hydrochloric acid. . . . .	18.2
Nitrous oxide. . . . .	22
Carbon dioxide. . . . .	22
Cyanogen. . . . .	26

But, while these figures express the relative weights of the molecules of the substances named, it can easily be shown that, if the atomic weight of hydrogen is 1, these figures do not express the molecular weights of the substances. Take hydrochloric acid, for example, The smallest molecular weight that can be assigned to this compound, if the atomic weight of hydrogen is 1, is 36.4, for hydrochloric acid consists of 1 part by weight of hydrogen combined with 35.4 parts by weight of chlorine. Hence, if the sum of the weights of its atoms or its molecular weight were less than 36.4, the weight of the atom of hydrogen would be less than 1. If the molecular weight of hydrochloric acid is 36.4 the molecular weights of the other substances named in the above table can easily be calculated, The results are as given in the subjoined table.



Substance.	Mol. Weight.
Hydrogen.....	2
Marsh-gas.....	16
Ammonia.....	17
Water.....	18
Hydrocyanic acid.....	27
Carbon monoxide.....	28
Nitric oxide.....	30
Hydrochloric acid.....	36.4
Nitrous acid.....	44
Carbon dioxide.....	44
Cyanogen.....	52

By determining the weight of a given volume of any substance in the form of gas or vapor it is therefore possible to determine the molecular weight of that substance.

**How are Atomic Weights Deduced from Molecular Weights?**—This can be illustrated by the case of oxygen. The substances in the above table that contain oxygen are water, carbon monoxide, carbon dioxide, nitric oxide, and nitrous oxide. These have all been analyzed and the results are given below:

Substance.	Mol. Wt.	Composition.
Water.....	18	2 pts. H + 16 pts. O
Carbon monoxide.....	28	12 " C + 16 " O
Carbon dioxide.....	44	12 " C + 32 " O
Nitric oxide.....	30	14 " N + 16 " O
Nitrous oxide.....	44	28 " N + 16 " O

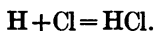
It will be seen that 16 is the smallest figure required to express the parts by weight of oxygen in any molecule. Now the molecular weights and composition of all oxygen

compounds that can be converted into vapor have been determined, and it has been found that the figure 16 is the smallest required to express the parts by weight of oxygen in any molecule. This figure is therefore selected as the atomic weight of oxygen. The atomic weights of other elements can be determined in the same way.

**Molecules of the Elements.**—The acceptance of Avogadro's hypothesis leads to a curious conclusion regarding the structure of elementary gases. The molecular weights of hydrogen, oxygen, chlorine, and nitrogen are found to be 2, 32, 70.8, and 28 respectively. According to this, these gases consist of molecules which are twice as heavy as their atoms, or, in other words, the molecules of these elementary gases consist of two atoms each. The same conclusion is reached in another way. When one volume of hydrogen combines with one volume of chlorine, two volumes of hydrochloric acid are formed. Now, as equal volumes of all gases contain the same number of molecules, if we assume that in a certain volume of hydrogen there are 100 molecules, then in the same volume of chlorine and of hydrochloric acid there are also 100 molecules. But from 1 volume containing 100 molecules of hydrogen and 1 volume containing 100 molecules of chlorine 2 volumes containing 200 molecules of hydrochloric acid are formed. In each molecule of hydrochloric acid gas there must be at least one atom of hydrogen and one atom of chlorine, and in the 200 molecules of hydrochloric acid there must be 200 atoms of hydrogen and 200 atoms of chlorine. These 200 atoms of hydrogen, however, must have been contained in the 100 molecules of hydrogen with which we started,

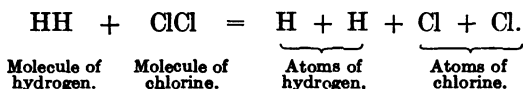
and similarly the 200 atoms of chlorine must have been contained in the 100 molecules of chlorine. Therefore, each molecule of hydrogen must consist of at least 2 atoms of hydrogen, and each molecule of chlorine must consist of at least 2 atoms of chlorine.

A similar study of other elementary gases leads to similar conclusions in regard to their molecules. The molecule of a few elementary gases has been shown to consist of 4 atoms, that of some of 3 atoms,\* and that of a few others of a single atom; but usually the condition is that found in hydrogen and chlorine. The view is thus forced upon us that the molecules of elementary gases consist of atoms of the same kind, just as the molecules of compound gases consist of atoms of different kinds. The molecule of hydrogen is composed of two atoms of hydrogen, just as the molecule of hydrochloric acid is composed of an atom of hydrogen and an atom of chlorine. According to this conception, when hydrogen gas and chlorine gas are brought together, the complete action is not represented by the equation

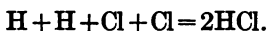


\* In speaking of ozone (page 75), it was stated that when oxygen is changed to ozone there is a diminution of volume from three to two without change of weight. In other words, the specific gravity of oxygen is two thirds that of ozone. But the specific gravity of oxygen leads to the conclusion that its molecule contains two atoms. Similarly, the specific gravity of ozone leads to the conclusion that its molecule contains three atoms. Ozone is therefore believed to be made up of molecules each of which consists of three atoms of oxygen; and ordinary oxygen to be made up of molecules each of which consists of two atoms of oxygen. The molecular weight of ordinary oxygen is 32, and that of ozone is 48.

The molecules of hydrogen and chlorine must be broken up before the act of combination can take place. Hence, there are two acts involved in passing from hydrogen gas and chlorine gas to hydrochloric acid. These are:



Then, further, the atoms combine to form compound molecules:



Or we may write the equation thus:



The process of dissociation, similar to ionization in solutions, probably plays an important part in the combination of gaseous substances.

Again, when an elementary gas such as hydrogen or oxygen is set free from a compound, it appears from the above that, at the instant it is liberated, it exists in the atomic condition, but that if there is nothing else present with which the atoms can combine, they combine with each other to form molecules. After it has been set free, therefore, it should be less active than at the instant it is set free. This is quite in accordance with many curious and well-known facts.

**Nascent State.**—It is found that at the instant elements are set free from their compounds they are capable of effecting changes which they cannot effect after they have once

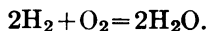
been set free. Thus, free oxygen gas passed into hydrochloric acid produces no change under ordinary conditions; but oxygen liberated from a compound in contact with hydrochloric acid decomposes the latter and sets chlorine free. Hydrogen gas passed into nitric acid causes no change; but hydrogen liberated in direct contact with nitric acid reduces the acid to ammonia. Many other examples of this kind of action might be cited. The simplest explanation of these phenomena is that offered above. An element at the instant of its liberation is said to be in the *nascent state*.

**Relation of Physics and Chemistry to Molecules.**—According to what has been said, all substances, elementary as well as combined, are made up of molecules. The molecules are believed to have the properties of the substance as we know it in the free state. The molecule is the smallest particle of a substance that can exist in the free state. The molecules are said to be held together by cohesion, and, theoretically, a substance could be separated into its molecules by purely mechanical processes. As long as action upon a substance does not involve decomposition of the molecules, the action is in the realm of physics. The molecules are made up of atoms. The atom enters into chemical action and is the largest particle of a substance that can do so. Chemistry is that science which has to deal with changes within the molecules. It must be remembered that these statements are not statements of facts known to us. The laws of definite and multiple proportions are statements of facts; but when we come to speak of atoms and molecules we are dealing with conceptions which, however probable they may appear, can nevertheless not be

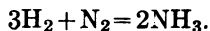
proved to be true. We make use of these concepts because they simplify our dealings with the facts of chemistry.

**Explanation of the Laws Governing the Combination of Gases.**—It has been pointed out (pages 174–175) that when hydrogen combines with chlorine, with oxygen, and with nitrogen the relations between the volumes of the combining gases are simple, and that these volumes in turn bear a simple relation to the volumes of the products formed. The explanation of these facts on the basis of Avogadro's hypothesis is as follows:

In equal volumes of hydrogen and of chlorine there is the same number of molecules. Each molecule of hydrogen and each molecule of chlorine consists of two atoms. When hydrogen and chlorine combine, one atom of one combines with one of the other, so that from one molecule of hydrogen and one of chlorine two molecules of hydrochloric-acid gas are formed. The number of molecules is the same after combination as before, and therefore the product occupies the same volume as the uncombined gases. When hydrogen combines with oxygen, however, two atoms of hydrogen combine with one of oxygen. The reaction is represented thus:



In this case two molecules of hydrogen and one molecule of oxygen give two molecules of water, and the volume of the product in the form of vapor is only two thirds that of the combining gases. The reaction between nitrogen and hydrogen is represented thus:



Or, from four molecules only two are obtained. Consequently the volume of the product is only half that of the uncombined gases.

**How a Formula is Determined.**—Chemical formulas were first introduced for the purpose of expressing the composition of substances. They might be used for this purpose at present without having any connection whatever with the conception of atoms and molecules, but the difficulty would then be to decide upon the combining weights of the elements. It would be possible for authoritative bodies to unite in issuing an edict that the combining weights of the elements shall be certain figures which are in harmony with facts known. But this would hardly be a scientific mode of procedure; and there might exist differences of opinion in regard to the advisability of accepting the figures. When, however, we once accept the atomic theory and the hypothesis of Avogadro, we have a definite basis to work on, and there is little opportunity for disagreement in regard to the figures to be adopted.

The necessary steps in the determination of the formula of a compound may be illustrated by the case of water. The compound is first analyzed and found to contain hydrogen and oxygen in the proportion of 1 part hydrogen to 8 parts oxygen. This is a fact. We wish, however, to express by our formula not only the composition of the substance, but the composition of a molecule of the substance. We therefore determine the molecular weight by the method described above by comparing the weight of its vapor with that of hydrochloric acid or hydrogen. We find that the molecular weight is 18. In other words, the

molecule of water, or the smallest particle of water, is 18 times heavier than an atom of hydrogen. According to the analysis, the 18 parts are made up of 2 parts of hydrogen and 16 parts of oxygen. By an examination of a large number of gaseous compounds containing oxygen we conclude that 16 is the atomic weight of oxygen, as the smallest weight of oxygen found in any of its compounds is 16 times heavier than the smallest weight of hydrogen found in any of its compounds. Therefore, the molecule of water consists of 2 atoms of hydrogen and 1 atom of oxygen. The formula representing the facts and conceptions in regard to the composition of water is  $H_2O$ .

**Raoult's Laws.**—Studies of solutions have shown that the following laws hold good:

1. *When weights of substances that are proportional to their molecular weights are dissolved in the same volume of a solvent, the same rise of the boiling-point is caused in each case.*

2. *When weights of substances that are proportional to their molecular weights are dissolved in the same volume of a solvent, the same lowering of the freezing-point is caused in each case.*

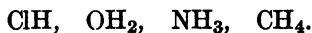
**Apparent Exceptions.**—These laws have been thoroughly tested and have been found to hold good in a large number of cases. In other cases, however, they do not at first sight appear to hold good. This is notably the case with acids, bases, and salts in solution in water. *In other words, the electrolytes are exceptions.* The explanation is believed to be this, that these substances are dissociated by water into ions, and each ion acts like a molecule so far as its effect



upon the boiling-point and the freezing-point of the solution is concerned. When a molecule of sodium chloride of the formula  $\text{NaCl}$  is dissolved in water it is broken down into the two ions  $\text{Na}$  and  $\text{Cl}$ , each of which produces the effect of a molecule upon the boiling-point and upon the freezing-point of the solution. It was to explain these apparent exceptions that the theory of electrolytic dissociation (see page 145) was suggested.

**Determination of Molecular Weights by the Boiling-point and the Freezing-point Methods.**—If Raoult's laws are true, it is plainly possible to determine the molecular weights of substances that are not dissociated by the solvent used. The details need not be given here. Suffice it to say that the methods are based upon observations on the boiling-points and the freezing-points of solutions.

**Valence.**—The formulas of the compounds thus far studied have all been determined by exactly the same methods. On comparing the formulas of the hydrogen compounds of chlorine, oxygen, nitrogen, and carbon, one cannot fail to be struck by certain curious differences between them. The formulas are



Speaking in terms of the theory, the molecule of hydrochloric acid consists of 1 atom of chlorine combined with 1 atom of hydrogen; the molecule of water consists of 1 atom of oxygen combined with 2 atoms of hydrogen; the molecule of ammonia consists of 1 atom of nitrogen combined with 3 atoms of hydrogen; the molecule of marsh-gas consists of 1 atom of carbon combined with 4 atoms

of hydrogen. It will thus be seen that the atoms of chlorine, oxygen, nitrogen, and carbon differ in their power of holding hydrogen in combination. The oxygen atom has twice the power of the chlorine atom, the nitrogen atom has three times this power, and the carbon atom has four times this power. An examination of the compounds of other elements shows that other atoms differ from one another in the same way.

The smallest power, so far as the number of other atoms which it can hold in combination is concerned, is that of the chlorine atom. And as one chlorine atom can hold but one atom of hydrogen in combination, so one atom of hydrogen can hold but one atom of chlorine in combination. Either the hydrogen atom or the chlorine atom may be taken as an example of the simplest kind of atom. An element like hydrogen and chlorine is called a *univalent element*; an element like oxygen whose atom can hold two unit atoms in combination is called a *bivalent element*; an element like nitrogen whose atom can hold three unit atoms in combination is called a *trivalent element*; an element like carbon whose atom can hold four unit atoms in combination is called a *quadrivalent element*. Most elements belong to one or the other of these four classes, though there are some which can hold five, six, and even seven unit atoms in combination. These are, however, rare, and for our present purpose they will require but slight notice.

*Valence* is that property of an element by virtue of which its atom can hold a definite number of other atoms in combination.

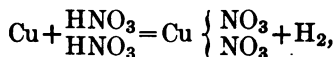
[Calcium forms with chlorine the compound  $\text{CaCl}_2$ . What is the valence of calcium? Potassium and sodium form

chlorides of the formulas  $KCl$  and  $NaCl$  respectively. What is the valence of these elements? Sulphur forms with hydrogen a compound of the formula  $SH_2$ . What is the valence of sulphur?]

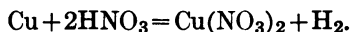
**Substituting Power of Elements.**—It has been shown that, in the formation of salts, metallic atoms are substituted for the hydrogen of acids. In such cases one atom of a univalent metal takes the place of one atom of hydrogen, one atom of a bivalent metal takes the place of two atoms of hydrogen, etc. Thus, potassium and sodium are univalent. An atom of either takes the place of one atom of hydrogen in forming salts. In the formation of potassium nitrate from nitric acid,  $HNO_3$ , one atom of potassium is substituted for the one atom of hydrogen in the molecule of nitric acid, forming the salt  $KNO_3$ . So, also, in sodium nitrate,  $NaNO_3$ , one atom of the univalent element sodium is substituted for one atom of hydrogen. In the molecule of sulphuric acid,  $H_2SO_4$ , there are two atoms of hydrogen. To replace these, two atoms of a univalent element are required. Thus, potassium sulphate is  $K_2SO_4$ , and sodium sulphate is  $Na_2SO_4$ . Examples of salts containing bivalent metals are the following: Zinc sulphate,  $ZnSO_4$ , in which one atom of the bivalent element zinc is substituted for the two atoms of hydrogen in sulphuric acid; and barium sulphate,  $BaSO_4$ , in which one atom of bivalent barium takes the place of the two atoms of hydrogen in sulphuric acid.

When a bivalent metal forms a salt with an acid like nitric acid, which contains but one atom of hydrogen in the molecule, it is believed that one atom of the metal acts

upon two molecules of the acid, thus:



or



The formula of zinc nitrate is similar, *viz.*,  $\text{Zn}(\text{NO}_3)_2$ . In the case of trivalent elements the matter is a little more complicated, but still simple enough if it is borne in mind that a univalent atom takes the place of one atom of hydrogen; a bivalent atom takes the place of two atoms of hydrogen; a trivalent atom takes the place of three atoms of hydrogen, etc.

**Variations in Valence.**—The subject of valence is a difficult one to deal with, for the reason that the valence of an element is not fixed, but varies according to conditions. It may vary (1) according to the temperature. In general, the higher the temperature the lower the valence. Thus, phosphorus, which is quinquivalent towards chlorine at ordinary temperatures, as is shown by the formation of the compound  $\text{PCl}_5$ , is trivalent towards the same element at higher temperatures, as is shown by the fact that when heated the compound  $\text{PCl}_5$  gives off chlorine and becomes  $\text{PCl}_3$ .

The valence of the element may vary (2) according to the chemical character of the element with which it combines. Thus, sulphur, which is sexivalent towards fluorine, as shown by the compound  $\text{SF}_6$ , is bivalent towards hydrogen, as shown by hydrogen sulphide,  $\text{SH}_2$ ; and phosphorus, which is quinquivalent towards chlorine at ordinary tem-

peratures, is trivalent towards hydrogen, as is shown by the compound  $\text{PH}_3$ .

Generally speaking, however, each element shows a tendency to act with a particular valence; or if it varies at all, the variation is between narrow limits. Nitrogen appears as trivalent and quinquivalent; carbon as bivalent and quadrivalent, etc.

**Summary.**—Avogadro's hypothesis that equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules was suggested by a comparison of the weights of equal volumes of gases, or their specific gravities, with the combining weights as found by analysis. The molecular weights of substances bear to one another the same relations as the specific gravities of their gases or vapors.

After analyzing the compounds of an element and determining their molecular weights, the smallest quantity of the element that occurs in any of the compounds is taken as the atom, and the weight of this quantity as compared with the weight of the smallest quantity of hydrogen found in any of its compounds taken as unity is the atomic weight of the element.

Elementary gases and vapors are made up of molecules, which in turn consist of atoms of the same kind. Elements are more active in the nascent state than in the free state, probably because the instant they are set free the atoms are uncombined, while after they have been set free these atoms are combined in the form of molecules.

Formulas of compounds are intended to represent the composition of molecules and their relative weights.

Raoult's laws concerning the relations between the weights of dissolved substances and the boiling-points and freezing-points of their solutions furnish a basis for the determination of the molecular weights of the substances in solution.

The valence of an element is the property by virtue of which its atom has the power of holding in combination a certain number of other atoms. Elements are called univalent, bivalent, trivalent, quadrivalent, etc., according as they exhibit the simplest valence like that of hydrogen and chlorine, or double, treble, or quadruple this valence.

The substituting power of the elements is determined by the valence. An atom of a univalent element can take the place of one atom of hydrogen; an atom of a bivalent element can take the place of two atoms of hydrogen; an atom of a trivalent element can take the place of three atoms of hydrogen, etc.

## CHAPTER XII.

### CARBON.

**Carbon in Plants and Animals.**—Most substances of vegetable or animal origin blacken when they are heated to a sufficiently high temperature, and if heated in the air they burn up. This is due to the fact that nearly all animal and vegetable substances contain the element carbon. When they are heated the other elements present are first driven off in various forms of combination, while the carbon is the last to go. If the heating is carried on in the air, the carbon finally combines with oxygen to form a colorless gas—it burns up. Carbon is the central element of organic nature. All living things contain this element as an essential constituent. The number of the compounds which it forms is almost infinite, and they present such peculiarities that they are commonly treated under a separate head, "Organic Chemistry." There is no good reason for this, except the large number of the compounds and the peculiarities of their chemical relations and reactions. For the present it will suffice to study the chemistry of the element itself, and of a few of its simpler compounds, and farther on a few chapters devoted to some of its most important compounds will be presented.

**Occurrence.**—From what has already been said, it will be seen that carbon occurs in nature for the most part in combination with other elements. It occurs not only in living things, but in their fossil remains, as in coal. Coal-oil, or petroleum, consists of a large number of compounds which contain only carbon and hydrogen. Most products of plant-life contain the elements carbon, hydrogen, and oxygen. Among the more common of these may be mentioned sugar, starch, cellulose, etc. Most products of animal life contain carbon, hydrogen, oxygen, and nitrogen. Among them may be mentioned albumin, fibrin, casein, urea, etc. Carbon occurs in the atmosphere in the form of carbon dioxide. [What evidence have we already had of the presence of carbon dioxide in the air? See pages 159, 160.] It also occurs in the form of salts of carbonic acid—the carbonates—which are widely distributed, forming whole mountain-ranges. Limestone, marble, and chalk are calcium carbonate.

Uncombined, the element occurs pure in two very different forms in nature: (1) as *diamond*, and (2) as *graphite*, or *plumbago*.

Before presenting the evidence that leads to the conclusion that diamond and graphite are only different forms of the same element, and that while closely related to each other they are also equally closely related to charcoal, it will be best to study separately the properties of each of these three substances.

**1. Diamond.**—The diamond is found in but few places on the earth. Little is known as to the conditions which gave rise to its formation. The celebrated diamond-beds



are in India, Borneo, Brazil, and South Africa. When found, diamonds are covered with an opaque layer, which must be removed before the beautiful properties appear. The crystals are sometimes what are known as octahedrons; that is to say, they are regular eight-sided figures, though usually they are somewhat more complicated. For use as a gem it must be cut and polished. The object in view is to bring out as strikingly as possible its brilliancy by exposing the faces favorably to the action of the light. It is the hardest substance known, and is utilized as points for the "diamond drills" employed in boring rock.

If heated to a very high temperature without access of air, it swells up and is converted into a black mass resembling graphite. This change takes place without loss in weight. Heated to a high temperature in oxygen, it burns up, yielding only carbon dioxide. It is insoluble in all ordinary liquids. It dissolves, however, in molten cast iron and in some other molten metals.

Moissan has made small diamonds by dissolving charcoal in cast iron in a crucible heated in an electric furnace, and then plunging the crucible into water. In this case the outside of the solution is quickly solidified while the inner portions are still liquid and under strong pressure. Under these circumstances the carbon is deposited from the solution in small diamonds.

**2. Graphite.**—Graphite, or plumbago, is found in nature in large quantities. Sometimes it is crystallized in soft plates or leaflets but in forms entirely different from those assumed by the diamond. It can be prepared artificially by dissolving charcoal in molten iron, from which solution

graphite is deposited on cooling. It can also be prepared by heating charcoal to a high temperature in the electric furnace. The variety thus obtained differs in some of its properties from that which crystallizes from iron. Both varieties are found in nature. Graphite has a grayish-black color and a metallic lustre. It is quite soft, leaving a leaden-gray mark on paper when drawn across it, and is hence used in the manufacture of so-called *lead* pencils. It is sometimes called black-lead.

When heated without access of air it remains unchanged. Heated to a very high temperature in the air, or in oxygen, it burns up, forming only carbon dioxide. Like the diamond, it is insoluble in all ordinary liquids.

The name graphite is given to different modifications of carbon. Between the soft, light Siberian graphite and the dense, heavy and very hard graphite used to make arc-light terminals, there are various modifications, differing in their physical properties. An artificial graphite is now prepared at Niagara Falls by Acheson's process. In this process coke is heated with a small proportion of iron in an electric furnace. The iron evaporates and the coke is converted into graphite.

**Uses of Graphite.**—Graphite is used for making lead pencils, stove polish, crucibles, as a lubricator, and for electrodes. It is one of the few materials which endures the temperature of the electric furnace, hence its use for crucibles. Its value as lubricator depends on its crystalline structure.

**Deflocculated Graphite.**—By treating powdered graphite

with tannic acid, Acheson obtains a modification of graphite which forms smooth emulsions with water, petroleum or oils, forming excellent lubricants for machinery.

**3. Amorphous Carbon.**—All forms of carbon that are not diamond or graphite are included under the name *amorphous carbon*. The name signifies simply that it is not crystallized. The most common form of amorphous carbon is ordinary charcoal.

**Charcoal** is made by the *charring process*, which consists simply in heating without a free supply of air. The substance almost exclusively used in the manufacture of charcoal is wood. As has already been stated, wood is made of a large number of substances, nearly all of which, however, consist of the three elements carbon, hydrogen, and oxygen. One of the chief constituents of all kinds of wood is cellulose. Now, when a piece of wood is heated to the kindling temperature in the air, it burns. The chemical changes that take place are complex under ordinary circumstances; but if care is taken, the combustion can be made complete, when all the carbon is converted into carbon dioxide, and all the hydrogen into water. If, on the other hand, the air is prevented from coming in contact with the wood in sufficient quantity to effect complete combustion, the hydrogen is given off partly as water and partly in the form of volatile compounds containing carbon and oxygen. Most of the carbon, however, is left behind as charcoal, as there is not enough oxygen to convert it into carbon dioxide.

**A Charcoal-kiln.**—A charcoal-kiln consists essentially of a pile of wood so arranged as to leave spaces between

the pieces. The pile is covered with a structure of brick-work or with some rough material through which the air will not pass easily, as, for example, a mixture of powdered charcoal, turf, and earth. Openings are left in this covering so that after it is kindled the wood will continue to burn slowly. The changes above mentioned take place, the gases or volatile substances passing out at the top of the kiln, and appearing as a thick smoke. In due time the holes through which the air gains access to the wood, and which also make the burning possible, are closed, and the burning stops. Charcoal, which is impure amorphous carbon, is left behind. As wood always contains some incom-bustible substances in small quantity, these are, of course, found in the charcoal. When the wood or charcoal is burned, these substances remain behind as the ash.

**Wood-charcoal.**—Ordinary charcoal is a black, comparatively soft substance. It burns in the air, though not easily unless the gases formed are constantly removed and fresh air is supplied, as when the draught is good or a pair of bellows is used. It burns readily in oxygen (see Experiment 22, page 31). The product of the combustion in oxygen and in air, when the conditions are favorable, is carbon dioxide,  $\text{CO}_2$ . In the air, when the draught is bad, another compound of carbon and oxygen, carbon monoxide,  $\text{CO}$ , is formed. Heated without access of air, charcoal remains unchanged. Charcoal is insoluble in all ordinary liquids.

**Coke.**—Besides wood-charcoal, there are other forms of amorphous carbon, which are manufactured for special purposes, or are formed in processes carried on for the sake

of other products. *Coke* is a form of amorphous carbon which is made by heating ordinary gas-coal without access of air, as is done on the large scale in the manufacture of coal-gas. Coke bears to coal about the same relation that charcoal bears to wood.

**Lampblack** is a very finely divided form of charcoal which is deposited on cold objects placed in the flames of burning oils. The oils consist almost exclusively of carbon and hydrogen. When burned in the air they yield carbon dioxide and water. If the flame is cooled down by any means, or if the supply of air is partly cut off, the carbon is not completely burned; the flame "smokes," and deposits soot. This soot is largely made up of fine particles of carbon. It is used in the manufacture of printer's ink. Carbon is acted upon directly by very few substances, and is not soluble, so that it is impossible to destroy the color of printer's ink without destroying the material upon which it is impressed.

**Boneblack, or Animal Charcoal**, is a form of amorphous carbon which is made by charring bones. Unless treated with an acid it contains the incombustible substances contained in bones, as calcium phosphate, etc.

**Charcoal Filters.**—Boneblack and wood-charcoal are very porous and have the power to absorb gases. When placed in air containing offensive gases, these are absorbed and the air is thus purified. When water containing disagreeable substances is treated with charcoal, these are wholly or partly absorbed and the water improved. Charcoal filters are therefore extensively used. A charcoal filter to be efficient should be of good size, and from time to time the

charcoal should be renewed. The small filters which are screwed into faucets are of little value, as the charcoal soon becomes charged with the objectionable material of the water.

Some coloring matters can be removed from liquids by passing the latter through *boneblack filters*. On the large scale, this fact is taken advantage of in the refining of sugar. The solution of sugar first obtained from the cane or beet is highly colored; and if it were evaporated, the sugar deposited from it would be dark colored. If, however, the solution is first passed through boneblack filters, the color is removed, and now, on evaporating, white sugar is deposited. In the laboratory constant use is made of this method for the purpose of purifying liquids.

#### FILTERING THROUGH CHARCOAL.

*Experiment 86.*—Make a filter of boneblack by fitting a paper filter into a funnel 12 to 15 cm. (5 to 6 inches) in diameter at its mouth. Half fill this with boneblack. Make a dilute solution of indigo. Pour it through the filter. If the conditions are right, the solution will pass through colorless.—Do the same thing with a dilute solution of ink.—If the color is not completely removed by one filtering, filter it again.—The color can also be removed from solutions by putting some boneblack into them and boiling for a time.—Try this with half a litre each of solutions of ink and indigo like those used in the first part of the experiment. Use about 4 to 5 grams boneblack in each case. Shake the solution frequently while heating.

**Wood is Charred to Preserve it.**—Charcoal does not suffer decay in the air or under water nearly as readily as wood. This is another way of stating the chemical fact that the substances of which wood is made up are more susceptible to the action of other chemical substances than charcoal is. The relative ease with which charcoal and wood burn

in the air illustrates this fact. Piles driven below the surface of water are charred to protect them from the action of those substances which cause decay. Most of the houses in Venice stand on piles of wood which have been charred. Oak stakes have quite recently been found in the Thames where, according to Tacitus, the Britons fixed stakes to prevent the passage of Cæsar and his army.

**Coal.**—Under this head are included a great many kinds of impure amorphous carbon which occur ready-formed in nature. Although an almost infinite number of kinds of coal are found, for ordinary purposes they are classified as *hard* and *soft coals*, or *anthracite* and *bituminous coals*. Then there are substances more nearly allied to wood called *lignite*, and those which represent a very early stage in the process of coal-formation, as, for example, *peat*.

A close examination of all of these varieties has shown that they have been formed by the gradual decomposition of vegetable material in an insufficient supply of air. The process has been going on for ages. Sometimes the substances have, at the same time, been subjected to great pressure, as can be seen from the position in which they occur in the earth. The products in the *earliest* ages of the coal-forming process are, naturally, more closely allied to wood than those in the later stages.

All forms of coal contain other substances in addition to the carbon. The soft coals are particularly rich in other substances. When heated they give off a mixture of gases and the vapors of volatile liquids. The gases are, for the most part, useful for illuminating purposes. The liquids form a black, tarry mass known as *coal-tar*, from which are

obtained many valuable compounds of carbon. The gases are passed through water for the purpose of removing certain impurities. This water absorbs ammonia and forms the *ammonia-water* of the gas-works, which, as has been stated (page 166), is an important source of ammonia.

**Diamond, Graphite, and Charcoal are Different Forms of the Element Carbon.**—An element is a kind of matter from which no simpler kind of matter can be obtained by any means known to chemists. From hydrogen nothing but hydrogen can be obtained, except by bringing it together with some other element or some compound; from nitrogen, nothing but nitrogen, etc. In the case of carbon the element appears in three forms which differ markedly from one another. It is difficult to believe that the soft, black charcoal and the dull, gray, soft graphite are chemically identical with the hard, transparent, brilliant diamond. Yet this is undoubtedly the case, as can be proved by a very simple experiment. Each of the substances when burned in oxygen yields carbon dioxide. Now, the composition of carbon dioxide is known, so that if the weight of carbon dioxide formed in a given experiment is known, the weight of carbon contained in it is also known. When a gram of pure charcoal is burned it yields  $3\frac{1}{2}$  grams of carbon dioxide, and in this quantity of carbon dioxide there is contained exactly 1 gram of carbon. Further, when a gram of graphite is burned the same weight ( $3\frac{1}{2}$  grams) of carbon dioxide is formed as in the case of charcoal; and the same is true of diamond. It follows from these facts that the three forms of matter known as charcoal, graphite, and diamond consist only of the element carbon.



[PROBLEM.—How much carbon dioxide,  $\text{CO}_2$ , should be obtained by burning 0.5 gram diamond? The atomic weight of carbon is 12.]

**Other Examples of the Occurrence of a Substance in Different Forms.**—That one and the same substance can appear in markedly different forms under different conditions is seen in the case of water. Hail and snow would hardly be suspected of being the same substance by one who was not quite familiar with them. The difference in this case, as in that under discussion, is believed to be due to the way in which the small particles of which the substances are made up are arranged with reference to one another. If we had a number of small pieces of wood all of the same size and shape, say cubical, and should carefully arrange these in some regular way, we might easily make a comparatively compact mass of them, and the mass would have a regular form. We might arrange them, further, in a second way with regularity. And we might simply throw the pieces together in a jumble. These three kinds of arrangement would represent, in a rough way, the difference between the three forms of carbon. Each pile would be made of wood, but still in outward appearance they would differ from one another.

**Common Properties of the Three Forms of Carbon.**—Notwithstanding the marked differences in their appearance, the three forms of carbon have, as we have seen, some properties in common. They are insoluble in all ordinary liquids. They are tasteless and inodorous. They are infusible. When heated without access of air, they remain unchanged, unless the temperature is very high.

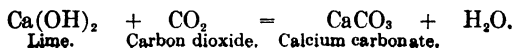
**Chemical Conduct of Carbon.**—At ordinary temperatures carbon is an inactive element. If it is left in contact with any one of the elements thus far studied,—*viz.*, hydrogen, oxygen, chlorine, and nitrogen,—no change takes place. Indeed, unless the temperature is raised it will not combine with any other element. At higher temperatures, however, it does combine with other elements, especially with oxygen, with great ease. Under some conditions it combines also with nitrogen, with hydrogen, and with many other elements. It combines with oxygen either directly, as when it burns in the air or in oxygen; or it abstracts oxygen from some of the oxides.

**Direct Union of Carbon and Oxygen.**—This has already been illustrated in Experiment 22, page 31, and is also illustrated in every charcoal-furnace. That carbon dioxide is the product may be shown by passing the gas into lime-water or baryta-water, when insoluble calcium, or barium, carbonate will be thrown down.

#### FORMATION OF CARBON DIOXIDE BY BURNING CHARCOAL.

*Experiment 86.*—Put a small piece of charcoal in a hard-glass tube. Pass oxygen through the tube, at the same time heating it. Pass the gases into clear lime-water. Arrange the apparatus as shown in Fig. 36.

*A* is a large bottle containing oxygen; *B* is a cylinder containing sulphuric acid; *C* is a U tube containing calcium chloride; *D* is the hard-glass tube containing the charcoal; *E* is the cylinder with clear lime-water. In what previous experiment was this method of showing the formation of carbon dioxide used? (See page 159.) The reason why it is used is that an insoluble compound is formed, and this can be seen, and it can be separated from the liquid and examined. The reaction is represented thus:



No other common gas acts in this way on lime-water. Hence, when, under ordinary circumstances, a gas is passed into lime-

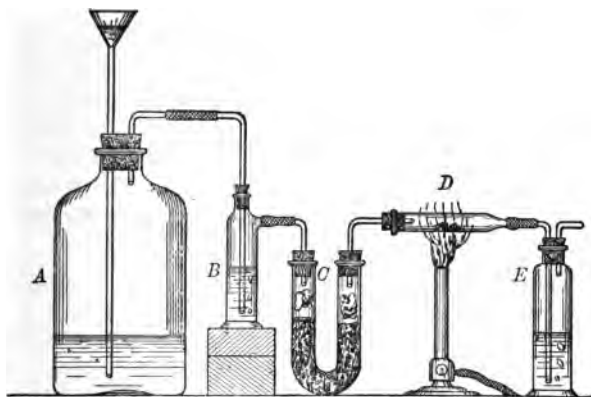


FIG. 36.

water and an insoluble substance is formed, we may conclude that the gas is carbon dioxide.

**Abstraction of Oxygen from Compounds by Means of Carbon.**—This can be illustrated in a number of ways.

#### DECOMPOSITION OF OXIDES BY CARBON.

*Experiment 87.*—Mix together 1 or 2 grams powdered copper oxide,  $\text{CuO}$ , and an equal bulk of powdered charcoal; heat in a hard-glass tube to which is fitted an outlet-tube, as shown in Fig. 37.

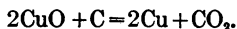
Pass the gas which is given off into lime-water contained in a test-tube. Is it carbon dioxide? What evidence have you that oxygen has been extracted from the copper oxide? What is the appearance of the substance left in the tube? Does it suggest the metal copper? Treat

a little of it with strong nitric acid. What should take place

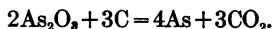


FIG. 37.

if the substance is metallic copper? (See Experiment 77, page 183.) What does take place? The reaction between the charcoal and the copper oxide is represented thus:



*Experiment 88.*—Perform a similar experiment with a little *white arsenic* in a small glass tube closed at one end. Take about equal parts of charcoal and arsenic. White arsenic is a compound of the element arsenic and oxygen, of the composition represented by the formula  $\text{As}_2\text{O}_3$ . The reaction that takes place when it is heated with charcoal is represented thus:



The element arsenic is volatile, and is hence driven upward and deposited on the inside of the tube above the mixture, in the form of a mirror with metallic lustre.

**Reduction.**—The abstraction of oxygen from a compound is known as *reduction*, as has already been explained. Hence carbon is called a reducing agent. It is indeed the reducing agent that is most extensively used in the arts. Its chief use is in extracting metals from their ores. Thus, iron does not occur in nature as iron, but in combination with other elements, especially with oxygen. In order to get the metal, the ore must be reduced, or, in other words, the oxygen must be extracted. This is accomplished by heating it with some form of carbon, either charcoal or coke.

[What other element already studied acts as a reducing agent? See pages 47, 67. Give an example of its reducing power.]

## CHAPTER XIII.

### SOME OF THE SIMPLER COMPOUNDS OF CARBON.

**Compounds of Carbon with Hydrogen.**—Carbon combines with hydrogen in a great many different proportions, the compounds being known as *hydrocarbons*. Among the simpler examples are *marsh-gas*, or *fire-damp*,  $\text{CH}_4$ ; *ethylene*,  $\text{C}_2\text{H}_4$ ; *acetylene*,  $\text{C}_2\text{H}_2$ ; and *benzene*,  $\text{C}_6\text{H}_6$ . These together with a few others will be taken up in a later chapter.

**Carbon Dioxide,  $\text{CO}_2$ .**—The principal compound of carbon and oxygen is carbon dioxide,  $\text{CO}_2$ , commonly called *carbonic-acid gas*. Under the head of The Air attention was called to the fact that this gas is a constant constituent of the air, though it is present in relatively small quantity. It issues from the earth in many places, particularly in the neighborhood of volcanoes. Many mineral waters contain it in large quantity, as the waters of Pymont, Selters, and the Geyser Spring at Saratoga. In small quantity it is present in all natural waters. In combination with bases it occurs in enormous quantities, particularly in the form of calcium carbonate,  $\text{CaCO}_3$ , varieties of which are ordinary limestone, chalk, marble, and calc-spar. Dolomite, a compound consisting of calcium carbonate and magnesium carbonate,  $\text{MgCO}_3$ , enters largely

into the structure of some mountain-ranges, as, for example, the Swiss Alps.

**Carbon Dioxide given off from the Lungs.**—Carbon dioxide is constantly formed in many natural processes. Thus, all animals that breathe in the air give off carbon dioxide from their lungs.

#### CARBON DIOXIDE FROM THE LUNGS.

*Experiment 89.*—Force the gases from the lungs for half a minute through some lime-water by means of an apparatus



FIG. 38

arranged as shown in Fig. 38. What is formed? Add a few drops of hydrochloric acid. What takes place?

**Carbon Dioxide formed in Combustion, in Decay, and in Fermentation.**—That carbon dioxide is formed in the combustion of charcoal and wood has already been shown. In a similar way it can be shown that the gas is formed whenever ordinary combustible materials are burned. From our fires, as from our lungs, and from the lungs of all animals, then, carbon dioxide is constantly given off. Further, the natural processes of decay of both vegetable

and animal matter tend to convert the carbon of this matter into carbon dioxide, which is then spread through the air. The process of alcoholic fermentation, and some other similar processes, also give rise to the formation of carbon dioxide. In all fruit-juices sugar is contained. When the fruits ripen, fall off, and lie exposed to the air, fermentation takes place, and the sugar is changed to alcohol and carbon dioxide. When carbonates are heated carbon dioxide is given off.

It is clear, therefore, that there are many important sources of supply of carbon dioxide, and it will readily be understood why the gas should be found everywhere in the air.

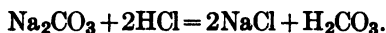
**Decomposition of Carbonates by Acids.**—The easiest way to get carbon dioxide unmixed with other substances is to add an acid to a carbonate. Whenever an acid is added to a carbonate there is an evolution of gas.

#### DECOMPOSITION OF CARBONATES BY ACIDS.

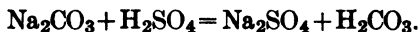
*Experiment 90.*—Put a little sodium carbonate in each of four test-tubes. Add to one a little dilute hydrochloric acid, to another a little dilute sulphuric acid, to a third a little dilute nitric acid, and to the remaining one a little dilute acetic acid. In each case pass the gas given off through lime-water; and insert a burning stick in the upper part of each tube.—Perform the same experiment with small pieces of marble.

**Comparison of this Decomposition with other similar Acts.**—The decomposition of the salts of carbonic acid by other acids affords another illustration of the principle that is involved in setting nitric acid free from a nitrate, or hydrochloric acid from a chloride, by means of sulphuric acid. The non-volatile acid drives out the volatile acid. When, for example, hydrochloric acid is added to sodium

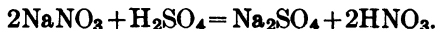
carbonate the first action consists in an exchange of the hydrogen of the acid for the metal of the carbonate:



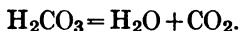
If sulphuric acid is used, the reaction is represented thus:



This reaction is analogous to that which takes place between sodium nitrate and sulphuric acid in the preparation of nitric acid:



Carbonic acid, however, is an unstable substance, and breaks down into water and carbon dioxide as soon as it is liberated from its salts:



As carbon dioxide is a gas it escapes.

It will be seen that the decomposition of carbonic acid into carbon dioxide and water is analogous to the decomposition of nitrous acid,  $\text{HNO}_2$ , into nitrogen trioxide and water; and to the decomposition of ammonium hydroxide into ammonia and water.

**Preparation of Carbon Dioxide.**—For the purpose of preparing carbon dioxide in the laboratory, calcium carbonate in the form of marble, or limestone, and hydrochloric acid are commonly used. The reaction involved is represented thus:





## PREPARATION OF CARBON DIOXIDE.

*Experiment 91.*—Arrange an apparatus as shown in Fig. 39. In the flask put some pieces of marble or limestone, and pour ordinary concentrated hydrochloric acid on it. The gas should be collected by displacement of air, the vessel being placed with the mouth upward, as the gas is much heavier than air. Collect several cylinders or bottles full of the gas. Into one introduce successively a lighted candle, a burning stick, a bit of burning phosphorus in a deflagrating-spoon. What takes place? With another proceed as if pouring water from it. Pour the invisible gas upon the flame of a burning candle. Pour some of the gas from one vessel to another, and show that it has been transferred. Weigh a beaker on a balance, and pour carbon dioxide into it. Give an account of the results obtained.



FIG. 39.

**Physical Properties of Carbon Dioxide.**—Carbon dioxide is a colorless gas. When subjected to a low temperature and high pressure it is converted into a liquid; and when some of the liquid is exposed to the air under suitable conditions, evaporation takes place so rapidly that a great deal of heat is absorbed, and some of the liquid becomes solid. The gas has a slightly acid taste and smell.

Carbon dioxide is much heavier than air, its specific gravity being 1.529. A liter of the gas under standard conditions of temperature and pressure weighs 1.971 grams. It dissolves in water, one volume of water dissolving about one volume of the gas at the ordinary temperature. As is the case with all gases, when the pressure is increased the water

dissolves more gas; and when the pressure is removed the gas escapes again. The so-called "soda-water" is simply water charged with carbon dioxide under pressure. The escape of the gas, when the water is drawn, is familiar to every one. The carbon dioxide used in charging the water is generally made from a sodium salt of carbonic acid known as "bicarbonate of soda" or from marble.

**Chemical Properties of Carbon Dioxide.**—Carbon dioxide is not combustible, nor does it support combustion. It is not combustible for the same reason that water is not; because it already holds in combination all the oxygen it has the power to combine with. Before it can burn again, it must first be decomposed. Carbon has the power to combine with oxygen, and in so doing it gives rise to the formation of a definite quantity of heat. One gram carbon burns to form carbon dioxide generating 8000 cal.:  $C + O_2 = CO_2 + 8000 \text{ cal.}$  A kilogram of carbon represents a definite quantity of energy, which we can get first in the form of heat and then convert into other forms, as electricity, motion, etc. After the kilogram of carbon has been burned, it no longer represents the energy it did in the form of carbon. A body of water elevated ten or fifteen feet represents a definite quantity of energy which can be obtained by allowing the water to fall upon the paddles of a water-wheel connected with the machinery of a mill. After the water has fallen, however, it no longer has power to do work, or it has no energy. In order that it may again do work, it must again be lifted. Not only does carbon dioxide not burn, but it does not support combustion. Although it contains a large quantity of oxygen in

combination, it does not as a rule give it up to other substances.

[What gas containing oxygen in combination with another element does support combustion?]

Commercially, the carbon dioxide that escapes from mineral springs, or is obtained as a by-product in chemical processes, is compressed in steel cylinders to the liquid form, and then placed on the market. Germany alone produced 11000 tons in a recent year. "Sparklets" are little steel capsules containing 2-4 grams liquid carbon dioxide, enough to make a bottle of soda water.

Cylinders of carbon dioxide are used for extinguishing fires. The small portable fire extinguishers generally contain a carbonate and a bottle of acid which breaks when a screw is turned; the acid falls on the carbonate generating carbon dioxide under pressure enough to direct the current of the gas with the hose.

**Respiration.**—It was stated above that carbon dioxide is given off from the lungs just as it is from a fire, and the fact was demonstrated by means of a simple experiment. It is a waste-product of the processes going on in the animal body. Just as it cannot support combustion, so also it cannot support respiration. It is not poisonous any more than water is; but it cannot supply the oxygen which is needed for breathing purposes, and hence animals die when placed in it. They die by suffocation, as they do in drowning. Any considerable increase in the quantity of carbon dioxide in the air above that which is normally present is objectionable, for the reason that it decreases the proportion of oxygen in the air which is breathed. It has been found

that as much as 5 per cent of pure carbon dioxide may be present in air without causing injury to those who breathe it. In a badly-ventilated room in which a number of people are collected and lights are burning, it is well known that in a short time the air becomes foul, and bad effects, such as headache, drowsiness, etc., are produced on the occupants of the room. These effects have been shown to be due, not to the carbon dioxide, as some have supposed, but to other waste-products which are given off from the lungs in the process of breathing. The gases given off from the lungs consist of nitrogen, oxygen, carbon dioxide, and water-vapor. Besides these, however, there are many substances in a fine state of division that contain carbon and are undergoing decomposition. These are poisonous, and are the chief cause of the bad effects experienced in breathing air which has become contaminated by the products from the lungs. As carbon dioxide is given off from the lungs at the same time, the quantity of this gas present is approximately proportional to the quantity of the organic impurities. Hence, by determining the relative quantity of carbon dioxide it is possible to determine whether the air of a room occupied by human beings is fit for use or not. As carbon dioxide is formed in the earth wherever an acid solution comes in contact with a carbonate, the gas is frequently given off from fissures in the earth. It is hence not infrequently found in old wells that have not been in use for some time, and deaths have been caused by descending into these wells for the purpose of repairing them. The gas is also frequently met with in mines, and is called *choke-damp* by the miners. The miners are aware that after an explosion caused by fire-damp there is danger of death from choke-damp. The

reason is simple. When fire-damp, or marsh-gas, explodes with air the carbon is converted into choke-damp, or carbon dioxide, and the hydrogen into water. Air in which a candle will not burn is not fit for breathing purposes.

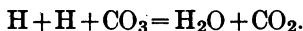
**The Cycle of Carbon in Nature.**—The part played by carbon dioxide in nature is extremely important and interesting. The carbon of living things is obtained from carbon dioxide, and returns to this form when life ceases. All living things contain carbon as an essential constituent. Whence comes this carbon? Animals eat either the products of plant-life or other animals which derive their sustenance from vegetable substances. The food of animals comes, then, either directly or indirectly from plants. But plants derive their sustenance largely from the carbon dioxide of the air. The plants have the power to decompose the gas with the aid of the direct light of the sun, and they then build up the complex compounds of carbon which form their tissues, using for this purpose the carbon of the carbon dioxide which they have decomposed. Many of these compounds are fit for food for animals; that is to say, they are of such composition that the forces at work in the animal body are capable of transforming them into animal tissues, or of oxidizing them, and thus keeping the temperature of the body up to the necessary point. That part of the food which undergoes oxidation in the body plays the same part as fuel in a stove. It is burned up with an evolution of heat, the carbon being converted into carbon dioxide, which is given off from the lungs. From fires and from living animals carbon dioxide is returned to the air, where it again serves as food for the plants. When

the life-process stops in the animal or plant, decomposition begins; and the final result of this, under ordinary circumstances, is the conversion of the carbon into carbon dioxide.

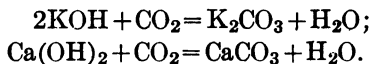
**Plants and Animals as Storehouses of Energy.**—Under the influence of life and sunlight carbon dioxide is, then, converted in the plant into compounds containing carbon which are stored up in the plant. These compounds are capable of burning, and thus giving heat; or some of them may be used as food for animals, assuming other forms under the influence of the life-process of the animals. As long as life continues, plants and animals are storehouses of energy. When death occurs, the carbon compounds pass back to the form of carbon dioxide; the energy which was stored up is lost. The power to do work which the carbon compounds of plants and animals possess comes from the heat of the sun. It takes a certain quantity of this heat, operating under proper conditions, to decompose a certain quantity of carbon dioxide and elaborate the compounds contained in the plants. When these compounds are burned they give out the heat which was absorbed in their formation during the growth of the plants. These compounds are said to possess chemical energy. This has its origin in heat, and is capable of reversion into heat. The transformation of the energy of the sun's heat into chemical energy lies at the foundation of all life. As the heat of the sun acting upon the great bodies of water and on the air gives rise to the movements of water which are essential to the existence of the earth as it is, so the action of the sun's rays on carbon dioxide, in the presence of the delicate mechanism of the leaf of the plant, gives rise to

those changes in the forms of combination of the element carbon which accompany the wonderful process of life.

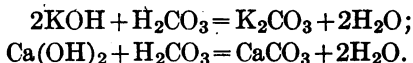
**Carbonic Acid and Carbonates.**—A solution made by passing carbon dioxide into water has a slightly acid reaction. [Try it.] It will act upon solutions of bases and form salts. The formula of the sodium salt formed in this way has been shown to be  $\text{Na}_2\text{CO}_3$ ; that of the potassium salt,  $\text{K}_2\text{CO}_3$ , etc. These salts are plainly derived from an acid,  $\text{H}_2\text{CO}_3$ , which is carbonic acid. It is probable that the ions of this acid are contained in the solution of carbon dioxide in water. These are, however, easily rearranged into carbon dioxide and water:



When carbon dioxide acts upon a base it forms a salt. Thus, with potassium hydroxide or calcium hydroxide, the action which takes place is represented thus:



With the acid the action would take place as represented thus:



#### FORMATION OF CARBONATES.

*Experiment 92.*—(tt) Pass carbon dioxide into a solution of caustic potash until it will absorb no more. Add an acid drop by drop to some of this solution and convince yourself that the gas given off is carbon dioxide. Write the equations representing the reactions which take place on passing the carbon dioxide into the solution of caustic potash, and on adding an acid to the resulting solution. What evidence have you that the gas is given off is carbon dioxide?

*Experiment 93.*—(tt) Pass carbon dioxide for a short time into 50 to 100 cc. clear lime-water. Filter off the white insoluble substance. Try the action of a little acid on it. What evidence have you that it is calcium carbonate? How could you easily distinguish between lime-water and a solution of caustic potash.

**Solution of Calcium Carbonate in Water containing Carbon Dioxide.**—Although when carbon dioxide is passed into lime-water calcium carbonate is at first precipitated, the calcium carbonate dissolves, and the solution finally becomes clear, if the gas is passed through it for some time. Water alone does not dissolve calcium carbonate, but water containing carbon dioxide does. If this solution is heated, the carbon dioxide is driven off and the calcium carbonate is again thrown down. Natural waters which flow over limestone take up more or less calcium carbonate by virtue of the carbon dioxide which they absorb from the air and the soil. Such waters, which are called *hard waters*, are in the condition of the solution of calcium carbonate above referred to. When heated, the calcium carbonate is deposited. This is frequently noticed in the deposits in boilers and other vessels in which hard water is boiled.

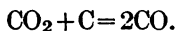
**CALCIUM CARBONATE DISSOLVED BY PASSING CARBON DIOXIDE INTO WATER CONTAINING IT.**

*Experiment 94.*—(tt) Pass carbon dioxide first through a little water to wash it, and then into clear lime-water. At first the insoluble carbonate will come down, as in Experiment 93; but soon it will begin to dissolve, and finally a clear solution will be obtained. Heat this solution, and the insoluble carbonate will again appear.

**Carbon Monoxide, CO.**—When a substance containing carbon burns in an insufficient supply of air,—as, for example,

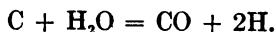


when the draught in a furnace is not strong enough to remove the products of combustion and supply fresh air,—the oxidation of the carbon is not complete, and the product, instead of being carbon dioxide, is carbon monoxide, CO. This substance can also be made by extracting oxygen from carbon dioxide. It is only necessary to pass the dioxide over heated carbon, when reaction takes place as represented thus:



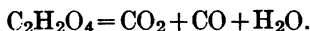
This method of formation is illustrated in coal-fires, and can be well observed in an open grate. The air has free access to the coal, and at the surface complete oxidation takes place. But that part of the carbon dioxide which is formed at the lower part of the grate is drawn up through the heated coal and is partly reduced to carbon monoxide. When the monoxide escapes from the upper part of the grate it again combines with oxygen, or burns, giving rise to the characteristic blue flame always noticed above a mass of burning coal. Should anything occur to prevent free access of air, carbon monoxide may easily escape complete oxidation.

It is also formed by passing steam over highly heated carbon, when this reaction takes place:



This is the reaction that is made use of in the manufacture of "water-gas." The gas thus obtained is a mixture of hydrogen and carbon monoxide. To make it useful for purposes of illumination it is "enriched" by passing it through a furnace in which it is mixed with highly-heated vapors of hydrocarbons from petroleum.

**Preparation of Carbon Monoxide.**—The easiest way to make carbon monoxide is to heat oxalic acid,  $C_2H_2O_4$ , with five to six times its weight of concentrated sulphuric acid. The change is represented thus:



Both carbon dioxide and monoxide are formed. Both are gases. In order to separate them the mixture is passed through a solution of caustic soda, which takes up the carbon dioxide [forming what?] and allows the monoxide to pass.

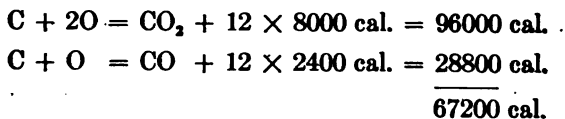
#### CARBON MONOXIDE.

*Experiment 95.*—Carbon monoxide is poisonous and must not be inhaled.—Put 10 grams crystallized oxalic acid and 50–60 grams concentrated sulphuric acid in an appropriate-sized flask. Connect with two Wouff flasks containing a solution of caustic soda. Heat the contents of the flask gently. Collect the gas over water in several vessels. Set fire to some, and notice the characteristic blue flame. What is formed when carbon monoxide burns in the air? Introduce the flame for a moment into a flask containing a little clear lime-water. What effect is produced?

**Properties of Carbon Monoxide.**—Carbon monoxide is a colorless, tasteless, inodorous gas, insoluble in water. It burns with a pale-blue flame, forming carbon dioxide. It is exceedingly poisonous when inhaled because its affinity for blood is 130 times as great as that of oxygen, and it decomposes the blood. Air becomes poisonous when it contains 0.05 per cent carbon monoxide. Hence it is very important that it should not be allowed to escape into rooms occupied by human beings. Death is sometime caused by the gases from coal-stoves. The most dangerous of these gases is carbon monoxide. A pan of smouldering

charcoal gives off this gas, the poisonous character of which is well known. It has been used to some extent for the purpose of suicide. The poisonous character of carbon monoxide has led to a great deal of discussion and to some legislation on the subject of "water-gas." The question has been repeatedly raised whether the manufacture of the gas should be permitted. There is no doubt of the fact that it is a dangerous substance; and that it should not be allowed to escape into the air of rooms is obvious. With proper precautions, however, there seems to be no good reason why it should not be used, although it is somewhat more poisonous than coal-gas.

**Thermochemistry of the Combustion of Carbon.**—One gram carbon burned to carbon dioxide yields 8000 cal. heat. One gram carbon burned to carbon monoxide yields 2400 cal. In terms of gram-molecular-weights these facts are expressed as below:



It will thus be seen that when carbon is burned to carbon monoxide, the product still contains more than two-thirds of the energy of the carbon. Hence the value of carbon monoxide in "fuel gases" (which see) and in metallurgical processes as a reducing agent.

## CARBON MONOXIDE A REDUCING AGENT.

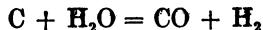
*Experiment 96.*—Pass carbon monoxide through a solution of caustic soda and then over some heated copper oxide contained in a hard-glass tube. Is the oxide reduced? How do you know? Is carbon dioxide formed? What evidence have you?

In the reduction of iron from its ores, the carbon monoxide formed in the blast-furnace plays an important part. At ordinary temperatures the gas does not combine readily with oxygen.

**Fuel Gases.**—The use of gaseous fuel is constantly on the increase in metallurgical and technical-chemical processes, because higher temperatures can be obtained by the rapid combustion of gas than by the slower combustion of coal or coke, and because both the temperature and the nature of the flame can be readily regulated.

While illuminating gas obtained by the distillation of coal has a high heat-value (calorimetric value), only a small portion of the coal distills, the greater part remaining as coke. It is an important problem to convert coal or coke completely into gas in such a way that the gas shall retain as much as possible of the heat-energy of the coal or coke. This is accomplished by making water-gas air-gas, Dowson-gas, generator-gas, etc.

As an example take the formation of water-gas:



Gram mol. wts.	12	18	28	2
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This process is endothermic, i. e. outside heat is required

to decompose the water in excess of that formed by the partial combustion of the carbon. As the heat absorbed by the decomposition of 18 grams water is exactly the same as the heat of combustion of 2 grams hydrogen the only final loss of heat is that expended in burning 12 grams carbon to 28 grams carbon monoxide:  $12 \times 2400 \text{ cal.} = 28000 \text{ cal.}$  to be deducted from the 96000 cal. total heat-energy of 12 grams carbon. But this heat is only lost when the gas is cooled to ordinary temperatures for transportation through pipes. If the hot gas is burned as fast as it is made, the loss of heat is not great; practically about 92 per cent of the fuel value of the coal is obtained from the gas.

"Air-gas" is made by conducting heated air over hot coke, and is a mixture of carbon monoxide and nitrogen. This process is exothermic, i. e. heat is given off.

**Siemens Regenerative Apparatus.**—The name refers to the regeneration of heat. The process consists in principle in utilizing waste heat to heat up cold air or gas before combustion, and in practice is applied in various ways. It is of great technical importance and is utilized in making gas, steel, glass, bricks, lime and many other products.

If in such an apparatus a *mixture* of air and steam in suitable proportions is passed over heated coal, the heat of the partial combustion of the coal in the air of the mixture is sufficient to decompose the steam without using other heat than that formed in the reaction. "Dowson-gas" and "generator-gas" are products formed in this way and contain carbon monoxide, hydrogen, and some hydrocarbons as valuable constituents, and nitrogen and carbon dioxide as worthless constituents.

"Oil gas" is made by dripping liquid by-products of the petroleum and paraffin industries into hot iron retorts. It has a high fuel value but is generally used as illuminant.

**Methods for Obtaining High Temperatures.**—The *calorimetric* value or amount of heat obtainable from a given substance must be distinguished from the *pyrometric* value or obtainable temperature. For example, a temperature sufficient to melt platinum ( $1700^{\circ}$ ) cannot be reached by burning coal or fuel gas, but platinum is readily melted by the heat of the oxy-hydrogen blowpipe, about  $2000^{\circ}$ . Temperatures of  $2500$ – $3000$  degrees can be obtained by the Goldschmidt process (which see), and much higher temperatures by the electric furnace which utilizes the heat of the electric arc.

**Electric Arc Furnace.**—Figure 40a represents a cross section of Moissan's electric furnace for laboratory use.

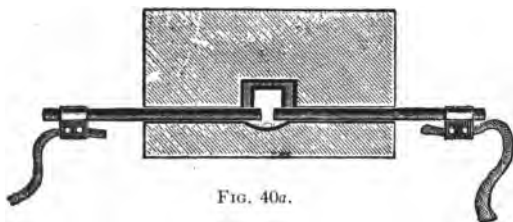


FIG. 40a.

Figure 40b represents the furnace in perspective.

This simple furnace is made of two blocks of limestone hollowed at the furnace space and grooved to admit the electrodes. The blocks are bound together by iron bands to prevent cracking.

**Technical Applications of the Electric Furnace.**—Large furnaces of varied type and construction, but all heated by the electric arc, are employed for making nitrates from atmospheric nitrogen, carborundum, artificial graphite, calcium carbide, calcium cyanamide, alloys of iron with other metals, and high grade steels. Cheap water-power to drive the dynamos is an essential. Sources of water-power situated on good transportation routes like Niagara

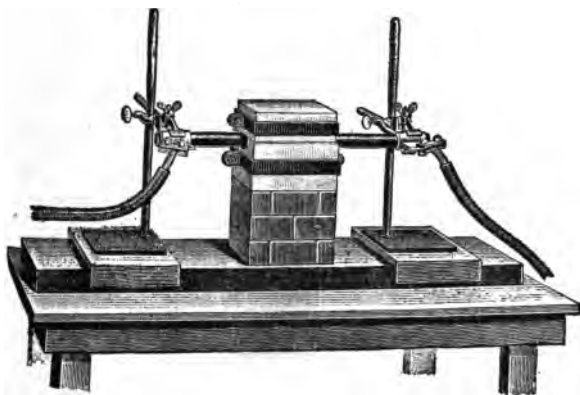


FIG. 406.

Falls were the first utilized. Now every year sees great industries established where water-power is available, often in regions hitherto remote from traffic or manufacture.

**Illumination, Flame, Blowpipe, etc.**—As the substances used for illumination contain carbon, and the chemical processes involved consist largely in the oxidation of the carbon of these compounds, this is an appropriate place to take up the subject of illumination, and also that of flame and the blowpipe.

In all ordinary kinds of illumination flames are the immediate source of the light. Whether illuminating-gas, a lamp, or a candle is used, the light comes from a flame. In the first case, the gas is burned directly; in the case of the lamp, the oil is first drawn up the wick, then converted into a gas, and this burns; while, finally, in the case of the candle, the solid material of the candle is first melted, then drawn up the wick, converted into gas, and the gas burns, forming the flame. In each case, then, there is a burning gas, and this burning gas is called a flame.

**Illuminating-gas.**—Two kinds of illuminating-gas are now made, *water-gas* and *coal-gas*. The method of preparation and the composition of the former have been given. The latter is made from coal by heating in closed retorts. When soft coal is heated the hydrogen passes off, partly in combination with carbon, as hydrocarbons, and partly in the free state. The nitrogen passes off as ammonia, and a large percentage of the carbon remains behind in the retort in the uncombined state as coke (see page 214). The gases given off are purified, and form ordinary illuminating-gas. One ton of coal yields on an average 10,000 cubic feet of gas. The value of gas depends upon the amount of light given by the burning of a definite quantity. It is measured by comparing it with the light given by a candle burning at a certain rate. The standard candle is one made of spermaceti, which burns at the rate of 120 grains an hour. The standard burner used for the gas is one through which 5 cubic feet of gas pass in an hour. Now, if it is desired to determine the illuminating-power of a gas, the gas is passed through the standard burner at the rate mentioned, and



the light which it gives is compared with the light given by the standard candle. The comparison is made by means of a so-called *photometer*. The illuminating-power of the gas is then stated in terms of candles. The statement that the illuminating-power of a gas is fourteen candles means that, when burning at the rate of 5 cubic feet an hour, its flame gives fourteen times as much light as the standard candle.

**Flames.**—Ordinarily when we speak of a flame we mean a gas which is combining with oxygen. The hydrogen flame is simply the phenomenon accompanying the act of combination of the two gases hydrogen and oxygen. Owing to the fact that we are surrounded by oxygen, we speak of hydrogen as the burning gas. How would it be if we were surrounded by an atmosphere of hydrogen? Plainly, oxygen would then be a burning gas. If a jet of oxygen is allowed to escape into a vessel containing hydrogen, a flame will appear where the oxygen escapes from the jet, if a light is applied. This is an experiment requiring great precautions, and, as the principle can be illustrated as well by means of illuminating-gas, we may use this instead. Just as illuminating-gas burns in an atmosphere of oxygen, so oxygen “burns” in an atmosphere of illuminating-gas.

#### BURNING OF OXYGEN.

*Experiment 97.*—(T) Break off the neck of a good-sized retort; fit a perforated cork to the small end; pass a piece of glass tube through the cork and connect by means of rubber hose with an outlet for illuminating-gas. Fix the apparatus in position, as shown in Fig. 40. Turn the gas on, and when the air is driven out of the retort-neck, light the gas. The neck is now filled with illuminating-gas, and the gas is burning at the mouth of the vessel.

If a jet from which oxygen is issuing is passed up into the gas the oxygen will take fire, and a flame will appear where the oxygen escapes from the jet. The oxygen burns in the atmosphere of coal-gas.

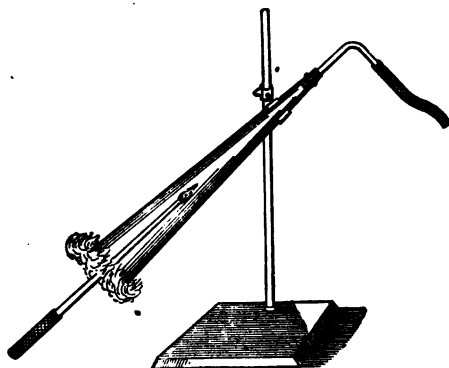


FIG. 40.

**Kindling-temperature of Gases.**—In studying the action of oxygen upon other substances, we learned that it is necessary that each of these substances should be raised to a certain temperature before it will burn. This statement is as true of gases as of other substances. When a current of hydrogen is allowed to escape into the air or into oxygen, no action takes place unless it is heated up to its burning-temperature, when it takes fire and continues to burn, as the burning of one part of the gas heats up the part that follows it, and hence the gas is heated up to the burning-temperature as fast as it escapes into the air. If the gas should be cooled down even very slightly below this temperature, it would be extinguished. This is shown in a very striking manner by the following experiments:

## COOLING A GAS PREVENTS IT FROM BURNING.

*Experiment 98.*—Light a Bunsen-burner. Bring down upon the flame a piece of fine brass or iron-wire gauze. There is no flame above the gauze. That the gas passes through unburned can be shown by applying a light just above the outlet of the burner and above the gauze. The gas will take fire and burn. By simply passing through the thin wire gauze, then, the gas is cooled down below its burning-temperature, and does not burn unless it is heated up again. Turn on a Bunsen burner. Do not light the gas. Hold a piece of wire gauze one and a half to two inches above the outlet. Apply a lighted match above the gauze. The gas will burn above the gauze, but not below it. Here again the heat necessary to raise the temperature of the gas to the burning-temperature cannot be communicated through the gauze. If in either of the above-described experiments the gauze is held in position for a time, it will probably become so highly heated that the gas on the side where there is no flame will be raised to the burning-temperature. The instant that point is reached the flame becomes continuous.

**Safety-lamp.**—The principle illustrated in the preceding experiments is utilized in the miner's *safety-lamp*. One of the dangers which the coal-miner has to encounter is the occurrence of fire-damp, or methane,  $\text{CH}_4$ , which with air forms an explosive mixture. The explosion can be brought about only by contact of flame with the mixture. In order to avoid the contact, the flame of the safety-lamp is surrounded by wire gauze, as shown in Fig. 41. When a lamp of this kind is brought into an explosive mixture of marsh-gas and air, the mixture passes

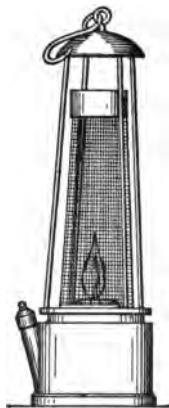


FIG. 41.

through the wire gauze and comes in contact with the flame, and a slight explosion occurs inside the gauze, but the flame of the burning gas inside the wire gauze cannot pass through and raise the temperature of the gas outside to the burning-temperature. Hence no serious explosion can take place. The flickering of the flame of the lamp, and the occurrence of small explosions inside, furnish the miner with information that he is in a dangerous atmosphere.

**Structure of Flames.**—The hydrogen flame consists of a thin envelope of burning hydrogen enclosing unburned gas, and surrounded by water-vapor, which is the product of the combustion. The structure of other flames depends upon the complexity of the gases burned and the conditions under which the burning takes place. In general, a flame consists of an outer envelope of gas combining with oxygen, and hence hot, and an inner part which contains unburned gas, which is relatively cool. A part of the unburned gas is, however, hot, and it would combine with oxygen were it not for the fact that it is surrounded by an envelope which prevents access of air. The *outer hot part* of the flame is called the *oxidizing flame*, because substances introduced into it are readily oxidized as they are heated to a high temperature in an atmosphere of oxygen. The *inner hot part* is called the *reducing flame*, because it consists of highly heated substances which have the power to combine with oxygen, and hence many compounds containing oxygen lose it, or are reduced, when introduced into this part of the flame. The hottest part of the flame is at the extreme top. Here oxidation is taking place most energetically. The hottest part of the unburned gases is at the tip of the

dark central part of the flame. In the flame of a Bunsen burner the two parts can be easily distinguished. The dark central part of the flame extends for some distance above the outlet of the burner. If the holes at the base of the burner are partly closed, the tip of the central part

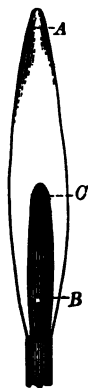


FIG. 42.

of the flame becomes luminous. This luminous tip is most efficient for the purpose of reduction. The principal parts of the flame are those marked in Fig. 42. *B* is the central cone of unburned gas. *C* is the luminous tip, the best part of the flame for reduction. *A* is the envelope of burning gas. This is further surrounded by a non-luminous envelope consisting of the products of combustion, carbon dioxide and water-vapor. Certain metals placed in the upper end of the flame take up oxygen, because they are highly heated in the presence of oxygen. Certain oxides lose their oxygen when placed in the tip of the central cone, because the gases are here heated to the temperature at which they have the power to combine with oxygen.

**Blowpipe.**—The oxidizing and reducing flames are frequently utilized in the laboratory. For the purpose of

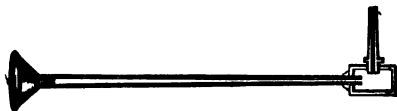


FIG. 43.

increasing their efficiency a *blowpipe* is used. This is a tube through which air is blown into a flame by means of the mouth. It is usually constructed in the shape shown in Fig. 43. At the smaller end, which is placed in the flame,

there is usually a small tube of platinum. The blowpipe may be used with the flame of a candle, an alcohol-lamp, or a gas-lamp. It is most frequently used with the gas-lamp as follows: A piece of brass tubing which fits snugly in the tube of a Bunsen burner is cut off and hammered together so as to leave a narrow slit-like opening. This tube is then slipped into the burner, as shown in Fig. 44.

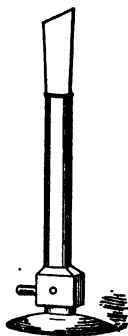


FIG. 44.



FIG. 45.

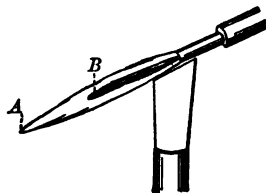


FIG. 46.

It reaches to the bottom of the burner, and thus cuts off the supply of air which usually enters the holes at the base. The gas is now lighted and the flow so regulated that there is a small flame about  $1\frac{1}{2}$  to 2 inches high. The tip of the blowpipe is placed on the slit of the burner in the flame, so that it extends about one third the way across it, as shown in Fig. 45. By blowing regularly and not too violently through the pipe the flame is forced down in the same direction as the end-piece of the blowpipe, and the slant of the burner-slit. Under proper conditions it separates sharply into a central blue part and an outer part of another color. The direction and lines of division of the flame are indicated in Fig. 46. The extreme outer tip *A* is the most effi-

cient oxidizing flame. The tip *B* of the inner blue part is the most efficient reducing flame.

The use of the blowpipe is illustrated by the following experiments:

#### THE BLOWPIPE.

*Experiment 99.*—Select a piece of charcoal about 4 inches long by 1 inch wide and 1 inch thick, with one surface plane.\* Near the end of the plane surface make a cavity by pressing the edge of a small coin against it, and turning it completely around a few times. Mix together equal small quantities of dry sodium carbonate and lead oxide. Put a little of the mixture in the cavity in the charcoal, and heat it in the reducing flame produced by the blowpipe. In a short time globules of metallic lead will be seen in the molten mass. After cooling, scrape the solidified substance out of the cavity in the charcoal. Put it into a small mortar, treat it with a little water, and, after breaking it up and allowing as much as possible to dissolve, pick out the metallic beads. [Is it malleable or brittle? Is metallic lead malleable or brittle? Is it dissolved by hydrochloric acid? Is lead soluble in hydrochloric acid? Is it soluble in nitric acid? Is lead soluble in nitric acid?] The action of the acids may be tried by putting the bead on a small dry watch-glass and adding a few drops of the acid. [Does the substance act like lead? What has become of the oxygen with which the lead was combined in the oxide? Is there any advantage in having a support of charcoal for this experiment?]

**EXPERIMENT 100.**—Heat a small piece of metallic lead on charcoal in the oxidizing flame of the blowpipe. Notice the formation of the oxide, which forms a coating or film on the charcoal in the neighborhood of the metal. [Is there any analogy between this process and the burning of hydrogen? In what does the analogy consist? What differences are there between the two processes?

\* Pieces of charcoal prepared for blowpipe work can be bought from dealers in chemical apparatus at small cost.

**Use of the Blowpipe in Analysis.**—Some oxides are easily reduced when heated in the reducing flame. Others are not. The composition of a substance can often be determined by heating it in the blowpipe flame and noticing its conduct. Some metals are easily oxidized in the oxidizing flame. Some form characteristic films of oxides on the charcoal, and in some cases it is possible to detect the presence of certain substances by noticing the color of the film of oxide. The blowpipe is therefore of great value as affording a means of detecting the presence of certain elements in mixtures or compounds of unknown composition. The chemical principles involved in its use will be clear from what has already been said.

**Causes of the Luminosity of Flames.**—It is evident from what has been seen that flames vary greatly in their light-giving power. The hydrogen flame, for example, gives practically no light. This is also the case with the flame of the Bunsen burner; while, on the other hand, the flame of illuminating-gas burning under ordinary circumstances, and that of a candle, etc., give light. To what is the difference due? There are several causes which operate to make a flame give light, and *vice versa*. In the first place, if a solid substance which does not burn up is introduced into a non-luminous flame, this solid substance becomes luminous. This is seen when a spiral of platinum wire is introduced into a hydrogen flame. It has also been shown by introducing a piece of lime into the hot non-luminous flame of the oxyhydrogen blowpipe. A similar cause operates in ordinary gas-flames to make them luminous. Particles of unburned carbon are always present, as can be shown by putting a piece of porcelain or any solid substance into



the flame, when there will be deposited on it a layer of soot which consists mainly of finely divided carbon. In the flame these particles of carbon are heated to the temperature at which they give light. Again, it has been found that the same candle gives more light at the level of the sea than it does when at the top of a high mountain, as Mont Blanc, on which the experiment was actually performed. This is partly due to a difference in the density of the gases. Naturally, the denser the gas the more active the combustion, the greater the heat, and the greater the light. This last statement ceases to be true when the oxidation becomes sufficient to burn up all the solid particles of carbon in the flame. If gases which in burning give light are cooled down before they are burned, the luminosity is diminished, and, conversely, non-luminous flames may be rendered luminous by heating the gases before burning them. When gases which give luminous flames are diluted to a sufficient extent with neutral gases, such as nitrogen and carbon dioxide, which neither burn nor support combustion, they become non-luminous. It has lately been shown that the formation and decomposition of acetylene (which see) in flames is an important factor in the luminosity of flames.

**Bunsen Burner.**—All the statements made in regard to the causes of the luminosity of flames are based upon carefully performed experiments. These experiments, however, cannot be easily repeated by the student in the laboratory in a satisfactory way. One constant reminder of the possibility of rendering a luminous flame non-luminous, and a non-luminous flame luminous, is furnished by the burner

universally used in chemical laboratories, and called, after the inventor, the *Bunsen burner*. The construction of this burner is easily understood. It consists of a base and an upper tube. The base is connected by means of a rubber tube with the gas-supply. The gas escapes from a small opening in the base, and passes up through the tube. At the lower part of the tube there are two holes, which can be opened or closed by turning a ring with two corresponding holes in it. When the gas is turned on, it is lighted at the top of the tube. Air is at the same time drawn through the holes at the base. The result is that the flame is practically non-luminous. If the ring at the base is turned so that the air-holes are closed, the flame becomes luminous. The advantage of the non-luminous flame for laboratory use consists in the fact that it does not deposit soot, and, at the same time, it does give a good heat.

[Could the hydrogen flame deposit soot?]

The non-luminosity of the flame of the Bunsen burner appears to be due to several causes: (1) Dilution of the gases by means of the nitrogen of the air; (2) Cooling of the gases by the entrance of the air; (3) Burning of the solid particles by the aid of the oxygen of the air admitted to the interior of the flame.

**Illuminants.**—These may be referred to three types: (A) Those in which the light is obtained from luminous flames; (B) Those in which the light is produced by heating solids to incandescence without combustion of the solid; (C) Those in which a solid becomes incandescent but burns without flame.

To class A belong candles, lamps, burning oil or petro-

leum, ordinary flames of coal-gas, water-gas, acetylene, oil-gas (or Pintsch-gas), etc.

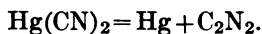
Class B includes the incandescent electric light—in which a carbon film or strip of metal is heated to incandescence in a vacuum by its resistance to the current—and the Welsbach light, in which a film of metallic oxides (see Thorium) is heated to incandescence by a non-luminous Bunsen flame from gas, alcohol, or petroleum.

Class C includes the different types of electric arc lamps, in which the glowing arc is formed between carbon terminals which glow and form carbon dioxide without flame.

The modern prodigal use of artificial light is noteworthy. More candles are manufactured now than at any former time. Indeed with the exception of animal and vegetable oils, every form of illuminant is in increasing demand in spite of the rapid increase in the number of illuminants.

**Cyanogen,  $C_2N_2$ .**—Carbon does not combine with nitrogen under ordinary circumstances. If, however, they are brought together at very high temperatures in the presence of metals, they combine to form compounds known as *cyanides*. Thus, when nitrogen is passed over a highly heated mixture of carbon and potassium carbonate,  $K_2CO_3$ , the compound potassium cyanide, KCN, is formed. Carbon containing nitrogen, as animal charcoal, when ignited with potassium carbonate, reduces the potassium carbonate, forming potassium, and this causes the carbon and nitrogen to combine, forming potassium cyanide. When refuse animal substances, such as blood, horns, claws, hair, wool, etc., are heated together with potassium carbonate and iron, a substance known as *potassium ferrocyanide*, or *yellow*

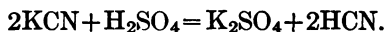
*prussiate of potash*,  $4\text{KCN} \cdot \text{Fe}(\text{CN})_2 + 3\text{H}_2\text{O}$ , is formed. When this is simply heated it decomposes, yielding potassium cyanide. It is not a difficult matter to make mercuric cyanide,  $\text{Hg}(\text{CN})_2$ , from the potassium compound. By heating mercuric cyanide it breaks down, yielding metallic mercury and cyanogen gas:



[What analogy is there between this reaction and that which takes place when mercuric oxide is heated?]

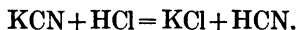
Cyanogen is a colorless gas. It receives its name from the fact that some of its compounds are blue (*κίανος*, *blue*). It is easily soluble in water and alcohol. It is extremely poisonous.

**Hydrocyanic Acid, Prussic Acid, HCN.**—This acid occurs in nature in combination with other substances,—in bitter almonds, the leaves of the cherry, laurel, etc. It is prepared by treating the cyanides with sulphuric or hydrochloric acid. Thus, by treating potassium cyanide with sulphuric acid this reaction takes place:



[What reactions already studied does this suggest?]

Further, by treating potassium cyanide with a solution of hydrochloric acid in water, hydrocyanic acid is liberated:



[Compare these reactions with similar reactions already studied.]

Hydrocyanic acid is a volatile liquid which boils at  $26.5^\circ$ ,

and solidifies at  $-15^{\circ}$ . It has a very characteristic odor, resembling that of bitter almonds. It is extremely poisonous. It dissolves in water in all proportions, and the solution is known as *prussic acid*.

Both cyanogen and hydrocyanic acid are extremely unstable. In the presence of water, the nitrogen tends to combine with hydrogen to form ammonia, and the carbon with oxygen and hydrogen to form stable compounds.

**Carbides** are compounds of carbon with metallic elements, such as calcium and aluminium. A good example is *calcium carbide* (which see).

**Summary.**—Carbon is contained in all living things, and in their fossil remains. The number of compounds which it forms is very large. They are usually treated together under the head of Organic Chemistry.

Carbon is found in the air in the form of carbon dioxide, and it is widely distributed in the earth in the form of carbonates.

Uncombined, it occurs in crystallized form in nature as diamond and graphite.

Amorphous carbon is a third variety of carbon. Charcoal in its various forms is amorphous carbon. It is made by charring organic substances which contain carbon, hydrogen, and oxygen. Coke, lampblack, and boneblack are other forms of amorphous carbon. Boneblack has the power to extract coloring matters from solutions. Charcoal has the power to absorb gases, and is used for purifying air. It also absorbs disagreeable substances from water, and is used for purifying water.

Coal is a form of carbon found in nature in many varieties.

The soft coals contain more hydrogen than the hard coals, which contain a larger percentage of carbon.

At ordinary temperatures carbon is a very inactive element. At high temperatures it combines with oxygen with avidity. It is hence a good reducing agent at high temperatures, and is used extensively as such in the extraction of metals from their ores.

Carbon forms a large number of compounds with hydrogen. These are the *hydrocarbons*.

Carbon dioxide is formed in many natural processes, as in respiration, combustion, decay, and fermentation. It is prepared by treating a carbonate with an acid. The gas given off is not carbonic acid, but a substance which bears to the acid the relation of an anhydride.

Carbon dioxide is the food of plants. Plants form the food of animals. Animals give back carbon dioxide to the air in the process of breathing. After death the carbon of animals and plants, if left exposed to the air, passes back largely to the form of carbon dioxide, and again starts on its round.

Carbon dioxide forms salts with bases. These have the general formula  $M_2CO_3$ , in which M represents a metal, such as potassium, sodium, etc. These are very unstable, being decomposed by any acid.

Calcium carbonate is insoluble in water, but it dissolves in water containing carbon dioxide. When heated the carbon dioxide is driven off and the calcium carbonate deposited. This phenomenon is the same as that which gives rise to the ordinary boiler incrustations.

Carbon monoxide is a poisonous gas, which is formed by incomplete oxidation of carbon or incomplete reduction of carbon dioxide. It is formed in ordinary coal-fires by the

passage of carbon dioxide over hot coal or charcoal. It combines readily with oxygen, and is hence a good reducing agent, as it contains three-fourths of the effective energy of the carbon it is a valuable fuel.

A flame is a burning gas. A gas that burns in oxygen will form an atmosphere in which oxygen will burn. If a burning gas is cooled down even very slightly below its burning-temperature, it is extinguished. In the miner's safety-lamp the flame is surrounded by a piece of wire gauze. The gas cannot pass through this gauze without being cooled down below the burning-temperature.

Flames are made up of different parts with different properties. The outer tip is the hottest part, and is called the oxidizing flame. The tip of the dark inner part, consisting of unburned gas, is the reducing flame.

A luminous flame can be made non-luminous by diluting the burning gas with neutral gases; by cooling the gases; by introducing oxygen into the gas so as to effect complete oxidation of the carbon.

In the presence of metals carbon and nitrogen combine to form cyanides. From these, cyanogen and hydrocyanic acid are obtained.

## CHAPTER XIV.

### CLASSIFICATION OF THE ELEMENTS.—PERIODIC LAW.

**General.**—It is difficult to classify the elements satisfactorily, for the reason that, if one set of properties is made the basis of classification, it is questionable whether there may not be more fundamental properties which should furnish the basis. As our knowledge in regard to the fundamental properties of the elements increases, the problem of classification will become simpler.

**Acid and Basic Properties.** — The chemical properties that force themselves upon the attention most prominently in every field of chemistry are those which are known as *acid properties* and *basic properties*. As has already been pointed out, these two kinds of properties are complementary. Whatever developments there may be in the study of chemistry in the future, it is certain that the distinction between these two kinds of properties will always be recognized as important. In general, both acids and bases contain oxygen and hydrogen. *There are some elements whose compounds with hydrogen and oxygen have basic properties, and others whose compounds with hydrogen and oxygen have acid properties.* This important fact may be used as the foundation of a partial classification of the elements. Accord-



ing to this, we have (1) *acid-forming elements* and (2) *base-forming elements*. As examples of the first class, the elements chlorine, nitrogen, and carbon, already studied, may be mentioned. Examples of the second class are sodium, calcium, magnesium, copper, iron, zinc, etc. The last-mentioned elements are generally called *metals*, and the acid-forming elements are generally called *non-metals*. The line between acid-forming and base-forming elements cannot be drawn sharply, for there are some elements that form both acids and bases, according to the relative quantity of oxygen with which they are combined. Thus, antimony forms acids with well-marked properties, and also other compounds which neutralize acids, and are therefore bases. The same is true of chromium, manganese, and some other elements. On the other hand, there are several elements that form only acids, and several that form only bases; and, further, those which form both acids and bases generally show a tendency in one direction. In dealing with the elements, then, these differences in properties will be taken into account.

**Natural Families of the Elements.**—Another important fact is that the elements fall into families according to their general chemical properties, the members of the same family showing striking resemblances to one another. Thus, there is the chlorine family, which includes, besides chlorine itself, bromine, iodine, and fluorine. It will soon be seen that these three elements resemble chlorine very closely, so that what has already been learned in regard to chlorine will be of great assistance in the study of the other members of the family. Further, there is the sulphur

family, consisting of the closely related elements sulphur, selenium, and tellurium; the potassium family, consisting of lithium, sodium, potassium, rubidium, and caesium; the calcium family, consisting of calcium, barium, strontium; and others. In all these cases the resemblance between the members of the same family is striking.

**Relations between Atomic Weights of the Elements and their Properties.**—It has long been known that in many cases there is a connection between the atomic weights of the elements and their properties. This is illustrated by the natural families of which chlorine, sulphur, sodium, and calcium are the best-known members. The members of the chlorine family most closely related to it are bromine and iodine; those of the sulphur family are selenium and tellurium. Similarly, sodium and lithium are related to potassium; and barium and strontium to calcium. The atomic weights of these elements are given in the table below:

Chlorine.. 35.4	Sulphur.. 32	Lithium.... 7	Calcium.... 40
Bromine.. 80	Selenium.. 79	Sodium.... 23	Strontium.. 87
Iodine... 127	Tellurium. 127	Potassium.. 39	Barium.... 137

It will be seen that the atomic weight of bromine is nearly the mean of those of the other two members of the family.

For,  $\frac{35.4 + 127}{2} = 81.2$ . The same relation holds in the other families:

$$\frac{32 + 127}{2} = 78.5; \quad \frac{7 + 39}{2} = 23;$$

and

$$\frac{40 + 137}{2} = 88.5.$$

Similar relations are met with throughout the list of chemical elements, and a thorough study of the subject has led to the remarkable conclusion that the connection between the atomic weights and properties of the elements is general. This was first shown by the Russian chemist Mendeléeff, the German chemist Lothar Meyer, and the English chemist Newlands.

**The Periodic Law.**—If, leaving out hydrogen and the inert elements occurring in air, and beginning with lithium, which next to these has the lowest atomic weight, the elements are arranged in the order of their atomic weights, the first fourteen exhibit a remarkable relation, as shown in this table:

Li-7;    Gl-9;    B-11;    C-12;    N-14;    O-16    F-19;  
Na-23;    Mg-24;    Al-27;    Si-28;    P-31;    S-32;    Cl-35.4.

The elements whose symbols stand in the same vertical column in this table have similar chemical properties. The resemblance is marked in the case of lithium and sodium; carbon and silicon; nitrogen and phosphorus; oxygen and sulphur; and fluorine and chlorine. Proceeding in the same way, the element with the next higher atomic weight is potassium, 39. This comes in the same vertical column with lithium and sodium or with members of the same family. Then follow calcium, scandium, titanium, vanadium, chromium, and manganese, each of which falls naturally in the vertical column containing elements allied to it. It has been found possible in this way to arrange all the elements except hydrogen—which, strange to say, finds no place in the system—in one table exhibiting the relations between their atomic weights and properties. Several tables have

been proposed, but they do not differ essentially from one another. The table on page 263 is a simple arrangement.\*

The eighth element, sodium, in the order of the increasing atomic weights is very much like lithium. So also the fifteenth element like the eighth resembles lithium. Up to and including manganese there are twenty-one elements excluding hydrogen. These fall naturally into three series of seven members each, and arranging the symbols of these horizontally, those elements that fall in the same vertical columns have the same general character. The three elements following manganese, *viz.*, iron, cobalt, and nickel, are very much alike, and they do not belong in any one of the main groups. The next element, copper, has some properties which ally it to the members of Group I. The next six elements fall in Groups II to VII and are in their proper places, and the next six fall in Groups I to VII, and are also in their proper places as far as their properties are concerned. After molybdenum in the sixth series comes a blank. There is no element known to fill that placé. It is, however, probable that there is one undiscovered, with the atomic weight approximately 100 and with properties similar to those of manganese. Then follow three elements which resemble one another as closely as iron, cobalt, and nickel. These do not belong in Groups, I, II, and III, but form a small independent group. These two groups of three elements occur at the end of the fourth and sixth series respectively. One would therefore naturally expect a simi-

\* In this table the approximate atomic weights are used instead of those which have been determined and calculated with the greatest care. For most purposes in the laboratory the approximate figures answer well enough, and they are commonly used.

MENDELÉEFF'S TABLE

SERIES	GROUP 0. R.	GROUP I. RH. R <sub>2</sub> O.	GROUP II. RII. RO.	GROUP III. RH <sub>2</sub> (?). R <sub>2</sub> O <sub>3</sub> .	GROUP IV. RII. RO <sub>2</sub> .	GROUP V. RII. R <sub>2</sub> O <sub>5</sub> .	GROUP VI. RH. RO <sub>3</sub> .	GROUP VII. RH. R <sub>2</sub> O <sub>7</sub> .	GROUP VIII. — RO <sub>4</sub> .
1		H=1							
2	He=4	Li=7	Gl=9.1	B=11	C=12	N=14	O=16	F=19	
3	Ne=20	Na=23	Mg=24.4	Al=27	Si=28	P=31	S=32	Cl=35.5	Fe=56, Ni=58.5,
4	A=39.9	K=39.1	Ca=40	So=44	Ti=48.1	V=51.3	Cr=52.3	Mn=55	Co=59.1, Cu=63.3.
5	—	(Cu)=63.3	Zn=65.4	Ga=69.9	Ge=72	As=75	Se=79	Br=80	Rh=103, Ru=103.8,
6	Kr=81.8	Rb=85.4	Sr=87.5	Y=89	Zr=90.7	Cb=94.2	Mo=95.9	—=100	Pd=108, Ag=107.9
7	—	(Ag)=107.9	Cd=112	In=118.7	Sn=118	Sb=120.3	Te=125.2	I=126.9	
8	Xe=128	Cs=132.9	Ba=137	La=138.5	Ce=141.5	—	—	—	
9	—	(—)	—	—	—	—	—	—	
10	—	—	—	Yb=173.2	—	Ta=182.8	W=184	—	Ir=193.1, Pt=194.8,
11	—	(Au)=196.7	Hg=200.4	Tl=204.1	Pb=206.9	Bi=208	—	—	Os=200, Au=196.7,
12	—	—	Ra=225	—	Th=233.4	—	U=239	—	

lar group at the end of the eighth series. No such group is known, though at the end of the tenth series, where we should naturally look for the next similar small group there are the three elements osmium, iridium, and platinum.

The elements of Series 2, beginning with lithium and ending with fluorine, differ in some respects quite markedly from the other elements of the groups to which they belong, as will be seen later. Beginning with sodium, it will be seen that there are two series of seven elements and a short series of three; then again two series of seven and a series of three; and, although the following series are imperfect, it is easy to recognize that the same general arrangement of the elements holds good to the end. A series of seven elements is called a *short period*: while two short periods with the accompanying three similar elements constitute a *long period*.

**Position of Elements which Show no Chemical Properties.**

—The Elements of Group 0 given in Mendeléeff's Table I show no chemical properties. Efforts to cause them to combine with other elements have thus far proved fruitless. Our knowledge of them is confined to their physical properties. They are all mon-atomic, i.e. contain but one atom in the molecule.

Their atomic weights place them as links between the extremely active non-metallic elements of Group VII and the extremely active metallic elements of Group I, a very suggestive position, showing in the series chlorine-argon-potassium for example, a complete extinction of chemical activity, an inert mon-atomic element midway between the active non-metal chlorine and the active metal potassium.

The remarkable relations thus presented are summed up in the *periodic law*;

*The properties of the elements are periodic functions of their atomic weights.*

**Acid-forming and Base-forming Elements.**—Those elements which have the strongest metallic character, whose hydroxides are the strongest bases, are included in Group I. The hydroxides of the metals in Group II are weaker bases, those of the elements in Group III are weaker still, while the hydroxides of some of the elements included in Group IV have weak acid properties and no basic properties. The elements of Group V are nearly all acid-forming. Those of Group VI form strong acids, as do those of Group VII.

**The Weight of its Atom Determines the Properties of an Element.**—If the atomic weight of an element is known, its position in the table is known, and from its position its properties can be stated with considerable accuracy. When the table was first constructed, the three elements scandium, gallium, and germanium were undiscovered. It was seen, however, that the gaps existed, and it was predicted that elements would be found with atomic weights approximately 44, 69, and 72 respectively, and that these elements would have certain properties which were clearly described. It was suggested that the element with the atomic weight 44 would bear to calcium and titanium about the same relation that aluminium bears to magnesium and silicon. The predictions were soon afterward confirmed, and the description of the element given before it was discovered was found to be singularly correct. The predictions in

regard to gallium and germanium were also verified most strikingly. Unquestionably the properties of the elements are determined by their atomic weights. An element whose atom weighs 100 times as much as that of hydrogen must have certain definite properties. It must combine with hydrogen and with oxygen in certain proportions; it must be allied to the members of the chlorine family; its properties are the result of that particular weight.

**Plan to be Followed.**—The elements hydrogen, oxygen, chlorine, nitrogen, and carbon have been studied in order to illustrate the methods of studying chemical problems in general, and as examples of the chemical elements. Now, following the suggestions of the periodic law, a number of other elements will be treated of as members of families or groups. Hydrogen does not belong to any group. Oxygen has peculiarities that distinguish it from most other elements, but it nevertheless resembles sulphur in many ways, and the two are treated together. Chlorine, as already stated, belongs to a group of which fluorine, bromine, and iodine are the other members. Nitrogen belongs to a group of which phosphorus, arsenic, and antimony are the other best-known members. Carbon also belongs to a group, silicon being the other well-known member. We therefore have the following groups first to deal with:

CHLORINE GROUP.	SULPHUR GROUP.	NITROGEN GROUP.	CARBON GROUP.
Chlorine,	Sulphur,	Nitrogen	Carbon,
Bromine,	Selenium,	Phosphorus,	Silicon.
Iodine,	Tellurium.	Arsenic,	
Fluorine.		Antimony,	
		Bismuth.	

The principal members of these groups are acid-forming



elements. They are generally called non-metals. In the nitrogen group, however, two of the members are both acid-forming and base-forming. There is a gradation in the properties from nitrogen to bismuth.

As the object of this book is to present concisely such facts as serve to illustrate the general character of chemical action and the general principles of the science of chemistry, it will not be necessary to go into details in dealing with these groups. One member of each group having been studied comparatively fully, the other members may be treated briefly. It will thus be possible to get a clearer idea of the principles of the science than by attempting to study a large number of facts the connection between which can be but dimly discerned, if discerned at all.

After the acid-forming elements have been studied, the base-forming elements will be taken up in a similar way; but, as will be seen, the chemistry of the acid-forming elements exhibits more variety, and is hence better adapted to the illustration of the general principles of chemistry than that of the base-forming elements, so that the latter need not be treated of as fully.

## CHAPTER XV.

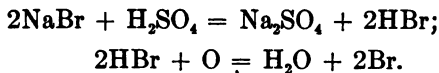
### THE CHLORINE GROUP: CHLORINE, BROMINE, IODINE, FLUORINE.

THE three members of this group which show the most marked resemblance are chlorine, bromine and iodine. Fluorine has properties of the same general kind, and its compounds resemble those of the other three members of the group, so that it is properly treated of with them.

**Bromine, Br (At. Wt. 80).**—This element occurs in nature in company with chlorine. Chlorine, as has been stated, occurs mostly in combination with sodium, as sodium chloride, or common salt. In several of the great salt-beds there is some bromine in the form of sodium bromide,  $\text{NaBr}$ , and in some places it occurs as magnesium bromide,  $\text{MgBr}_2$ , especially in the great beds at Stassfurt. The chief source of bromine in the United States is the mother-liquors from the salt-works, especially in Michigan, Southern Ohio and West Virginia. When a solution containing a large quantity of sodium chloride and a small quantity of the bromide is evaporated, the chloride is first deposited, and from the mother-liquors the bromide mixed with chloride is deposited.

**Preparation.**—The process of preparation of bromine in the laboratory is the same as that made use of for preparing chlorine (see page 111). It will be remembered that in order to get chlorine from sodium chloride the salt is

first converted into hydrochloric acid, and this is then oxidized. So, too, in order to get bromine from sodium bromide, it is first converted into hydrobromic acid, and this then oxidized. The reactions involved are usually:



As in the case of chlorine, the oxidizing substance commonly used is manganese dioxide, when the reaction takes place according to the following equation:



[Refer back to the explanation of this reaction given under the head of Chlorine. What other methods might be used in the preparation of bromine?]

**Uses.**—Bromine and its compounds are used in photography, in medicine, and to some extent in the manufacture of coal-tar colors.

**Manufacture of Bromine.**—Bromine is made in Germany from the Stassfurt deposits, and in the United States. In 1905 Germany produced 700 tons and the United States 596 tons. In Germany bromine is obtained from the mother-liquors of carnallite,  $\text{MgCl}_2\text{K}$ , (magnesium potassium chloride containing magnesium bromide) in the manufacture of potassium hydroxide. In this process the potassium chloride is separated from magnesium chloride and

bromide by crystallization and is then electrolyzed, forming potassium hydroxide and chlorine. This chlorine either as gas or liquefied is used to set free the bromine, which is then driven out of the solution by a current of steam:



This process is also used in the United States.

**Properties.**—Bromine is a heavy dark-red liquid at ordinary temperatures. It is easily converted into vapor which is brownish red. At  $-7.3^\circ$  it is solid. It has an extremely disagreeable smell, to which fact it owes its name (from *βρῶμος*, a stench).

Its properties are, in general, like those of chlorine. It acts violently upon organic substances. It attacks the skin and the membranes lining the passages of the throat and lungs in much the same way as chlorine. Wounds caused by the liquid coming in contact with the skin are painful and serious. It must be handled with great care. It dissolves slightly in water, forming a colored solution called bromine-water.

A substance called "solidified bromine" is made by soaking sticks of certain porous earthy materials in bromine.

The chemical conduct of bromine is also like that of chlorine. It combines with many elements directly and with great avidity. Its combination with arsenic and some other elements is accompanied by an evolution of light and heat, as in the case of chlorine. Its compounds with other elements are called *bromides*. While acting in general in the same way as chlorine, it is a somewhat weaker element, so that chlorine drives it out of its compounds and sets it free.

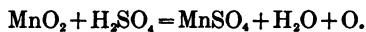
## BROMINE.

*Experiment 101.—Do not inhale the vapors!* Mix together 3.5 grams potassium bromide and 7 grams manganese dioxide. Put the mixture into a 500-cc. flask; connect with a condenser (see Fig. 22, page 69). Mix 15 cc. concentrated sulphuric acid and 90 cc. of water. After the liquid is cool pour it upon the mixture in the flask. Heat gently. Bromine will be given off in the form of vapor. A part of this will condense and collect in the receiver. Perform this experiment under a hood with a good draught. In treating the manganese dioxide and potassium bromide together with sulphuric acid, the action takes place as represented in the following equation:



Hence both potassium sulphate,  $\text{K}_2\text{SO}_4$ , and manganese sulphate,  $\text{MnSO}_4$ , are left behind in the flask.

[When sulphuric acid acts upon manganese dioxide at a high temperature the action takes place thus:



If this action took place in the presence of hydrobromic acid, what effect would the liberated oxygen have? Suppose the oxygen were allowed to escape from the flask containing the manganese dioxide and sulphuric acid, and then passed into hydrobromic acid, would the same result be reached as when the hydrobromic acid is in the flask from which the oxygen is liberated? What is the commonly accepted explanation? If the formula of manganese sulphate is  $\text{MnSO}_4$ , what is the valence of manganese? What would you expect the formula of manganese chloride to be? Of manganese oxide? Is the valence of manganese greater toward oxygen or toward chlorine?]

**Hydrobromic Acid, HBr.**—The only compound that bromine forms with hydrogen alone is hydrobromic acid. This is in all respects very much like hydrochloric acid.

It is made in the same way. It is a colorless gas that fumes in the air in consequence of its attraction for moisture. Its solution in water acts very much like ordinary hydrochloric acid. The elements are not held together as firmly in hydrobromic as in hydrochloric acid. This is shown by its decomposition under circumstances in which hydrochloric acid is stable. Thus, for example, it is decomposed by sulphuric acid, while hydrochloric acid is not. The hydrogen is separated from the bromine and acts upon the sulphuric acid, while the bromine is given off as such. Hence, when potassium bromide is treated with sulphuric acid, hydrobromic acid is given off, together with bromine, and a compound of sulphur and oxygen which is formed by the action of hydrogen on the sulphuric acid.

#### ACTION OF SULPHURIC ACID ON POTASSIUM BROMIDE.

*Experiment 102.*—In a small porcelain evaporating-dish put a few crystals of potassium bromide. Pour upon them a few drops of concentrated sulphuric acid. The white fumes of hydrobromic acid and the reddish-brown vapor of bromine are noticed. Treat a few crystals of potassium or sodium chloride in the same way. What difference is there between the two cases?

**Compounds with Hydrogen and Oxygen.**—With hydrogen and oxygen bromine forms compounds that resemble very closely those which chlorine forms with the same elements. The principal ones are *bromic* and *hypobromous acids*. The potassium salt of bromic acid,  $\text{HBrO}_3$ , is formed by treating a strong solution of caustic potash with bromine:



The potassium salt of hypobromous acid,  $\text{HBrO}$ , is formed by treating a dilute solution of caustic potash with bromine:



**Iodine, I** (At. Wt. 127).—This element occurs in nature in combination with sodium, in company with chlorine and bromine, but in smaller quantity than either. It is also found in larger quantities in all sea-plants. It is obtained largely from the latter source. On the coast of Scotland and France the seaweed which is thrown up by storms is gathered, dried, and burned. The organic portions are thus destroyed [What is the meaning of the word *destroyed* used in this sense?] and the mineral or earthy portions are left behind as ashes. This incombustible residue, which is called *kelp*, contains sodium iodide. Seaweed is also cultivated for the sake of the sodium iodide contained in it.

It also occurs in the great beds of soda saltpetre, or sodium nitrate, which are found in Chili, South America. It occurs in small quantity in combination with silver, and also in combination with lead and with mercury; and in the thyroid glands of human beings and other animals.

Iodine is obtained from sodium iodide, just as chlorine and bromine are obtained from their compounds with sodium and potassium. [Give the equations representing the steps which must be taken in order to separate iodine from sodium iodide.]

#### PREPARATION OF IODINE.

*Experiment 103.*—Mix together about 2 grams of sodium or potassium iodide and 4 grams manganese dioxide. Treat with a little concentrated sulphuric acid in a one- to two-litre flask.

Heat gently on a sand-bath. Gradually the vessel will be filled with the beautiful colored vapor of iodine. In the upper parts of the flask some of the iodine will be deposited in the form of crystals of a grayish-black color.

**Commercial Production of Iodine.**—In 1905, 300 tons of iodine were made from Chili saltpetre, and 294 tons from kelp, Scotland producing 130 tons, Japan 90, France 50, and Norway 24. There are different processes for treating the seaweed; the most scientific are those in which the fresh weed is allowed to ferment in tanks till it begins to rot and is then burned. In the fermentation alkaline sulphides and hydrogen sulphide are formed from organic sulphur compounds in the weed; the hydrogen sulphide reduces the organic iodine compounds to hydriodic acid which acts on the alkaline sulphides to form iodides. Iodides are not volatilized by burning the weed. The yield of iodine is tripled by this process.

The mother-liquor of Chili saltpetre contains 22 per cent sodium iodate. Iodine is obtained from it by reduction with sodium sulphite and sodium bisulphite:



The iodine is precipitated and is then purified by sublimation.

**Properties.**—At ordinary temperatures iodine is a grayish-black crystallized solid. It is volatile at ordinary temperatures. It acts upon the mucous membranes, though less energetically than chlorine and bromine. It colors the skin yellowish brown. It melts at 113–115°, and boils at 250°, when it is converted into a violet vapor.



Tincture of iodine acts as a counter-irritant on bruises and sprains. Goitrous swellings of the throat are caused by a lack of the normal iodine compound which is present in the thyroid glands of persons in health. The thyroid gland of the sheep is particularly rich in this compound which is called *thyroidine*, and contains 9.3 per cent of iodine. It is now extracted from the sheep glands and used as a remedy for goitre.

The action of iodine is, in general, the same as that of chlorine and bromine, only its action is weaker. Hydrobromic acid, as we have seen, is a weaker compound than hydrochloric acid. Hydriodic acid is still weaker. Chlorine acting upon hydrobromic acid sets bromine free. Chlorine and bromine set iodine free from hydriodic acid.

Iodine dissolves slightly in water, easily in alcohol, and easily in a water-solution of potassium iodide.

#### SOLUTIONS OF IODINE.

*Experiment 104.*—Make solutions of iodine in water, in alcohol, and in a water-solution of potassium iodide. Use small quantities in test-tubes.

When a solution containing *free iodine* is treated with a little starch-paste, the solution turns blue, in consequence of the formation of a complex compound of starch and iodine. Bromine and chlorine do not form blue compounds. Advantage is taken of this fact to distinguish iodine from the other members of the same family.

#### ACTION OF STARCH-PASTE ON IODINE.

*Experiment 105.*—Make some starch-paste by covering a few grains of starch in a porcelain evaporating-dish with cold water,

grinding this to a paste, and pouring 200-300 cc. boiling-hot water on it.\* Boil for 1 or 2 minutes. After cooling add a little of this paste to a dilute water-solution of potassium iodide to which has been added a very little iodine. The solution will turn blue. Now add a little of the paste to a dilute water-solution of potassium iodide. There is no change of color, because the iodine is in combination with the potassium. Add a drop or two of a solution of chlorine in water, when the blue color will appear. The explanation of this phenomenon is that the chlorine sets the iodine free, and the free iodine then acts upon the starch, producing the blue compound. [How can you show that the chlorine itself will not form a blue compound with starch?]

**Uses.**—Iodine is used in medicine and in the manufacture of dyes, and in photography. It is used mostly in the form of potassium iodide.

**Hydriodic Acid, HI,** is analogous to hydrochloric and hydrobromic acids. It is set free from its compounds by treating them with sulphuric acid, but it is even more unstable than hydrobromic acid, and hence breaks down into hydrogen and iodine. The iodine is liberated, while the hydrogen acts on the sulphuric acid, as it does in the case of hydrobromic acid.

#### ACTION OF SULPHURIC ACID ON POTASSIUM IODIDE.

*Experiment 106.*—Treat a few crystals of potassium iodide with sulphuric acid. [What do you notice?] Compare the result with that obtained in the case of potassium bromide and sodium chloride.

\*The purest form of starch found in the market is that made from arrowroot. Ordinary starch contains other substances some of which may interfere with the reaction with iodine.

It has been seen that hydrochloric acid is a stable substance, and that hydriodic acid is unstable, and that it requires less chemical energy to decompose hydriodic acid than hydrochloric. It also requires less heat energy. When one gr. mol. wt. hydrochloric acid in aqueous solution is decomposed, 39,300 calories heat are absorbed, while for one gr. mol. wt. hydriodic acid 13,100 calories are absorbed.

**Electrical Energy Required to Electrolyze Different Electrolytes.**—If different amounts of chemical energy and heat energy are required to decompose these acids it may be inferred that different amounts of electrical energy would be required. This is the case.

Electrical energy is the product of two factors, the amount of electricity and the electro-motive force or difference in potential, the unit of the latter being the volt. The *amount* of electricity may be compared with the volume of water in a stream passing a given point, the difference in potential with the fall or pressure of the water at that point.

If the fall of water on a water-wheel in a saw-mill gives just pressure enough to saw a log one foot in diameter, an attempt to saw a log two feet in diameter stops the wheel.

A current of an electro-motive force of 0.53 volts suffices to electrolyze hydriodic acid. An attempt to electrolyze hydrochloric acid with this current would stop the flow of electricity, a current of 1.41 volts electro-motive force being required to electrolyze hydrochloric acid.

While according to Faraday's first law, the *amount* of electricity required to electrolyze one equivalent of every

electrolyte is the same, the *electro-motive force* required and hence the *electric energy* required is greater or less according to the stability of the electrolyte.

**Iodic Acid,  $\text{HIO}_3$ .**—The principal compound of iodine with hydrogen and oxygen is iodic acid,  $\text{HIO}_3$ , which corresponds to chloric and bromic acids. It is known principally in the form of its potassium salt, potassium iodate,  $\text{KIO}_3$ . When heated, this salt, like the chlorate and the bromate, gives up all its oxygen, potassium iodide,  $\text{KI}$ , being left behind.

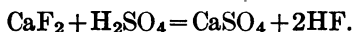
**Fluorine, F (At. Wt. 19).**—This element occurs in nature in large quantity, and widely distributed, but always in combination with other elements. It is found chiefly in combination with calcium, as *fluor-spar*, or *calcium fluoride*,  $\text{CaF}_2$ , and in combination with sodium and aluminium, as *cryolite*, a mineral which occurs abundantly in Greenland and has the composition  $3\text{NaF}.\text{AlF}_3$ , being a complex compound of sodium fluoride and aluminium fluoride.

All attempts to obtain fluorine in the free state failed until a few years ago, when its isolation was effected by passing an electric current through liquid hydrofluoric acid containing potassium fluoride in solution in a vessel of platinum-iridium.

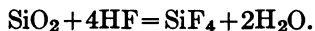
**Properties.**—Fluorine is the most active of all the elements at ordinary temperatures. It is a greenish-yellow gas. It acts upon almost all substances. Thus, it decomposes water, yielding ozone and hydrofluoric acid; at ordinary temperatures it combines directly with sulphur, phos-

phorus, iron, etc., with evolution of light and heat. It does not, however, act upon platinum.

**Hydrofluoric acid**, HF, is made from fluor-spar by treating it with sulphuric acid. The action is of the same kind as that which takes place when hydrochloric acid is liberated from sodium chloride: •



It is a colorless gas, with strong acid properties. *It greatly irritates the membranes lining the respiratory organs, and hence care should be taken not to inhale it.* It acts upon glass, dissolving it, and must therefore be kept in vessels of rubber, lead, or platinum, upon which it does not act. Its action on glass consists in the transformation of silicon dioxide or silica,  $\text{SiO}_2$ , which is contained in all kinds of glass, into *silicon tetrafluoride*,  $\text{SiF}_4$ , which is a gas. The action is represented thus:



#### HYDROFLUORIC ACID.

*Experiment 107.*—In a lead or platinum vessel put a few grams (5–6) of powdered fluor-spar and pour upon it enough concentrated sulphuric acid to make a thick paste. Cover the surface of a piece of glass with a thin layer of wax or paraffin, and through this scratch some letters or figures, so as to leave the glass exposed where the scratches are made. Put the glass over the vessel containing the flour-spar, and let it stand for some hours. Take off the glass, scrape off the coating, and the figures which were marked through the wax or paraffin will be found *etched* on the glass.

The acid is used for etching glass, especially for marking scales on thermometers, barometers, and other graduated glass instruments. A solution of the gas in water is manufactured for this purpose and kept in rubber or paraffin bottles.

Fluorine does not combine with oxygen. This is also true of helium and argon.

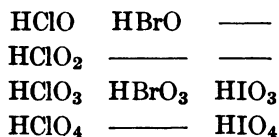
**Comparison of the Members of the Chlorine Group.**—In considering, first, the physical properties of these elements, we notice that all form colored gases or vapors. At ordinary temperatures chlorine is a gas, bromine a liquid, and iodine a solid. In regard to their chemical conduct, it may be said that, in general, fluorine is the most energetic; chlorine comes next in order, then bromine, and lastly iodine. This is seen especially in the relative stability of their compounds with hydrogen. Their compounds with metals also show the same relation. On the other hand, with oxygen the order is reversed. Fluorine does not unite with oxygen at all. The compounds of chlorine and oxygen are very unstable; those with bromine rather stable; and one compound of iodine and oxygen is comparatively stable.

The elements of this group combine with hydrogen and with other elements in the simplest way. *They are all univalent.*

The compounds formed by the three elements chlorine, bromine, and iodine with hydrogen and oxygen have analogous composition, and are formed by analogous reactions. Thus, we have the hydrogen compounds:

HCl, HBr, and HI;

and the compounds with hydrogen and oxygen:



The properties of any compound of one element are similar to those of the compounds of analogous composition of the other elements of the group.

All these facts seem to indicate that these elements are not distinct forms of matter entirely independent of one another, but rather that they contain some common constituent. The relations between the atomic weights of the members of the group have already been referred to.

## CHAPTER XVI.

### THE SULPHUR GROUP: SULPHUR, SELENIUM, TELLURIUM.

**Sulphur**, S (At. Wt. 32).—Sulphur is the principal member of this group. In nature it is frequently found accompanied by small quantities of selenium, and sometimes by tellurium. It has been known in the elementary form from the earliest times, for the reason that it occurs abundantly in this form in nature. It is found in Sicily and in several localities in the United States, especially in Louisiana, Nevada, and Utah, particularly in the neighborhood of volcanoes, as in Sicily. It occurs, further, in combination with many metals as sulphides,—as in iron pyrites,  $\text{FeS}_2$ ; copper pyrites,  $\text{FeCuS}_2$ ; galenite,  $\text{PbS}$ , etc.; in combination with metals and oxygen as sulphates—for example, as calcium sulphate, or gypsum,  $\text{CaSO}_4 + 2\text{H}_2\text{O}$ ; barium sulphate, or heavy spar,  $\text{BaSO}_4$ ; lead sulphate,  $\text{PbSO}_4$ ; in a few vegetable and animal products in combination with carbon, hydrogen, and, generally, with nitrogen.

**Extraction of Sulphur from its Ores.**—When taken from the mines, sulphur is mixed with earthy substances from which it must be separated. This separation is accom-



plished by piling the ore in such a way as to leave passages for air. The piles are covered with material to prevent free access of air, and the mass is then lighted below. A part of the sulphur burns, and the heat thus furnished melts the rest of the sulphur. The molten sulphur runs down to the bottom of the pile, and is drawn off from time to time. If the pile were not protected from free access of air, the sulphur would burn up, yielding a gas, sulphur dioxide,  $\text{SO}_2$ .

[What analogy is there between this process and that employed in making charcoal? What are the essential differences between the two processes?]

The above method is the one that has long been used in Sicily. It has been improved of late by the introduction of coal as fuel. In the United States hot water under pressure is used to melt the sulphur. It is not only extracted from the earth by this means but is thus obtained in pure condition.

**Refining of Sulphur.**—The crude brimstone obtained as above indicated is afterwards refined by distillation, and it is this distilled sulphur which comes to market under the names “roll brimstone” and “flowers of sulphur.” The distillation is carried on in earthenware retorts connected with large chambers of brickwork. When the vapor of sulphur first comes into the condensing-chamber it is suddenly cooled, and hence deposited in the form of a fine powder. This is called ‘flowers of sulphur.’ After the distillation has continued for some time, the vapor condenses in the form of a liquid, which collects at the bottom of the chamber. This is drawn off into wooden moulds and takes the form of “roll brimstone” or “stick sulphur.”

**Properties.**—Sulphur is a yellow, brittle substance which at  $-50^{\circ}$  is almost colorless. It melts at  $114.5^{\circ}$ , forming a thin, straw-colored liquid. When heated to a higher temperature it becomes darker and darker in color, and at  $200^{\circ}$  to  $250^{\circ}$  it is so viscid that the vessel in which it is contained may be turned upside down without danger of its running out. Finally, at  $448.4^{\circ}$  it boils and is then converted into a brownish-red vapor.

#### SULPHUR.

*Experiment 108.*—Distil about 10 grams of roll sulphur from an ordinary glass retort. Notice the changes above described. Collect the liquid sulphur which passes over, in a beaker-glass containing cold water.

**Crystals of Sulphur.**—When molten sulphur solidifies, or when it is deposited from a solution, its particles arrange themselves in regular forms called crystals. But, strange to say, the crystals formed from molten sulphur are entirely different from those deposited from solutions of sulphur. The former are honey-yellow needles. The latter are octahedrons with rhombic base, which is also the form of the sulphur found in nature. A careful examination of the needles shows that the angles which their faces form with one another are not the same as the angles formed by the faces of the octahedrons, and that the crystals are constructed on a different plan. The needles belong to the *monoclinic system* of crystals, and the octahedrons to the *rhombic system*.

**Crystallography.**—Notwithstanding the infinite number of forms assumed by solids in passing from the liquid to the solid state and when deposited from solutions, it has

been shown that all can be referred to a very few systems. Usually six systems are adopted. These are:

1. **THE REGULAR SYSTEM.** All the crystals belonging to this system can be referred to three axes of equal length, and at right angles to one another, crossing at the centre. Examples of crystals belonging to this system are the regular octahedron and the cube. The three axes are the imaginary lines which pass through the solid angles of the octahedron. All the other forms of this system may be referred to this octahedron.

2. **THE TETRAGONAL SYSTEM.** In this the forms are referred to three axes at right angles, two of equal length and one differing from the other two. The fundamental forms are the octahedron and prism.

3. **THE HEXAGONAL SYSTEM.** The crystals of this system are referred to four axes,—three of equal length inclined at  $60^\circ$  to one another, and a fourth at a right angle to them, which is either of the same length or of a different length. The six-sided pyramid and prism are the principal forms.

4. **THE RHOMBIC SYSTEM.** The crystals belonging to this system have three axes, of unequal lengths, at right angles to one another.

5. **THE MONOCLINIC SYSTEM.** In this system the crystals have three axes,—two at right angles to each other, the third at right angles to one and inclined to the other.

6. **THE TRICLINIC SYSTEM.** The crystals belonging to this system are referred to three axes, all inclined to one another.

[It would be well to have a set of models of the principal forms of the six systems of crystals available, and to study these until the general principles of the classification are

clear. Examples of crystals, either such as occur in nature or such as are made artificially, should also be studied, and the system to which they belong determined.]

The subject of crystallography is one that cannot be made clear in a few words. It requires careful study and much practice in observing forms of crystals. From what has just been said, however, it will be seen that the system of classification of crystals is a simple one. For our present purpose, the fact should be specially emphasized that the crystalline form of a substance is a definite property, by means of which it may be distinguished from other substances. The fact that a substance crystallizes in the regular system is just as characteristic of that substance as the fact that it boils or melts at a certain point. Thus, we know that ice always melts at  $0^{\circ}$ , and that water solidifies at  $0^{\circ}$ . We should be much surprised to find water solidifying at some other temperature, say  $20^{\circ}$ . Similarly, knowing that sulphur occurs in nature crystallized in forms which belong to the rhombic system, we are naturally surprised to find that, when molten sulphur solidifies, it crystallizes in forms belonging to the monoclinic system. What is perhaps still stranger is the fact that when the honey-yellow needles are allowed to stand unmolested they spontaneously undergo a change. They become opaque; their color changes; and now, if examined carefully, they are found to consist of minute crystals like those found in nature. It is evident that the arrangement of the particles in the monoclinic crystals of sulphur is not a stable one at ordinary temperatures, though it is stable above  $100^{\circ}$ .

Substances that crystallize in two distinct forms are called *dimorphous*. Carbon crystallizes in two different forms [What are they?], and is hence dimorphous.

## CRYSTALLIZATION OF SULPHUR.

*Experiment 109.*—In a covered porcelain crucible melt a few grams of roll sulphur. Do not heat higher than is necessary to melt the sulphur. Let it cool slowly, and when a thin crust has formed on the surface make a hole through this and pour out the liquid part of the sulphur. The inside of the crucible will be found lined with honey-yellow needles which, as has been stated, belong to the monoclinic system. Take out a few of the crystals and examine them. Are they brittle or elastic? What is their color? Are they opaque, transparent, or translucent? Lay the crucible aside, and in the course of a few days again examine the crystals. What changes, if any, have taken place?

**Other Forms of Sulphur.**—Sulphur can also be obtained in the amorphous, or uncrystallized, condition. That which was collected under water in Experiment 108 will be found to be soft and doughlike. It is amorphous. After a time it becomes brittle. When separated from a compound which is dissolved in water, it is finely divided, and gives the liquid an appearance suggesting milk.

**Crystallization from Carbon Bisulphide.**—Sulphur is insoluble in water, slightly soluble in alcohol and ether. It dissolves in carbon bisulphide,  $CS_2$ , and from the solution it is deposited in rhombic crystals.

## CRYSTALLIZATION OF SULPHUR FROM CARBON BISULPHIDE.

*Experiment 110.*—Dissolve 2 to 3 grams roll sulphur in 5 to 10 cc. carbon bisulphide. Filter through a fluted filter. Put the solution in a shallow vessel, and allow the carbon bisulphide to evaporate by standing in the air. The sulphur will remain behind in the form of crystals.

**Chemical Conduct of Sulphur.**—Sulphur combines with oxygen when heated to a sufficiently high temperature, forming sulphur dioxide,  $\text{SO}_2$ . [Compare carbon and sulphur in this respect.] It combines readily with most metals, forming sulphides, which are analogous to the oxides. Its combination with iron has already been shown in Experiment 10 (page 13). It also combines with copper, the act being accompanied by light and heat.

#### ACTION OF SULPHUR ON COPPER.

*Experiment 111.*—In a dry wide test-tube heat to boiling enough sulphur to form a layer about an inch thick. Introduce into the vapor small pieces of copper-foil or sheet-copper. Or hold a narrow piece of sheet copper so that the end just dips into the boiling sulphur.

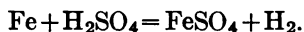
**Uses of Sulphur.**—Sulphur finds extensive use in the manufacture of sulphuric acid (page 298), matches, gun-powder (which see), ultramarine (which see), carbon bisulphide (page 303), in the process of vulcanization of rubber, in combating vine-disease in grape-growing countries, and in making solutions of sulphurous acid, of sodium thiosulphate, etc.

**World's Production of Sulphur.**—In 1901, 603,483 tons of sulphur were produced, of which Italy produced 563,096 tons and the United States only 6,976 tons. In 1906, owing to the development of the Louisiana deposits, 298,859 tons were produced in the United States.

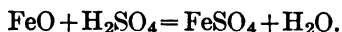
**Hydrogen Sulphide, Sulphuretted Hydrogen,  $\text{H}_2\text{S}$ .**—When hydrogen is passed over highly heated sulphur, the

two elements combine to form hydrogen sulphide. [Is there any analogy between this process and the formation of water by the burning of hydrogen?] This compound of sulphur and hydrogen occurs in nature in solution in the so-called sulphur waters, which are met with in many parts of this and other countries. It also issues from the earth in some places. It is formed by heating organic substances that contain sulphur, just as water is formed by heating organic substances that contain oxygen, and ammonia by heating such as contain nitrogen. It is formed, further, by decomposition of organic substances that contain sulphur, as, for example, the albumin of eggs. The odor of rotten eggs is partly due to the formation of hydrogen sulphide.

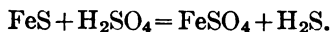
**Preparation.**—In the laboratory the gas is most readily made by treating a sulphide with an acid. When a metal, as iron, is treated with sulphuric acid, hydrogen is given off and the iron salt of the acid is formed thus:



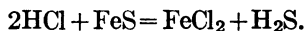
When sulphuric acid acts upon the oxide of iron, hydrogen is given off in combination with oxygen as water, thus:



Finally, when sulphuric acid acts upon iron sulphide, hydrogen is given off in combination with sulphur as hydrogen sulphide, thus:



A similar explanation holds for other acids. For example, hydrochloric acid acts upon iron sulphide in accordance with the equation



#### PREPARATION OF HYDROGEN SULPHIDE.

*Experiment 112.*—(tt) Arrange an apparatus as shown in Fig. 47. Put a small handful of iron sulphide,  $\text{FeS}$ , in the flask, and pour dilute hydrochloric acid upon it. Pass the evolved gas through a little water contained in the wash-cylinder A. Pass

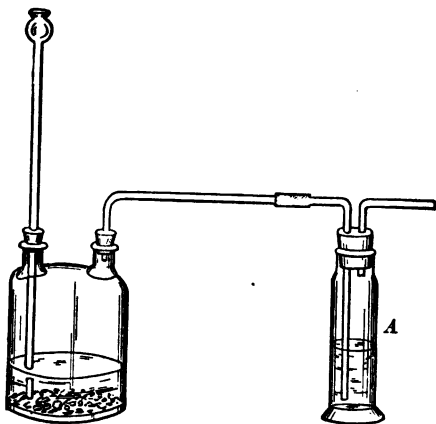
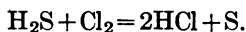


FIG. 47.

some of the gas into water. [What evidence have you that it dissolves?] Collect some by displacement of air. Its specific gravity is 1.178. [Should the vessel be placed with the mouth down or up?] Set fire to some of the gas contained in a cylinder. If there is free access of air, the sulphur burns to sulphur dioxide and the hydrogen to water.

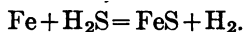


**Properties.**—Hydrogen sulphide is a colorless, transparent gas of specific gravity 1.178. It has an extremely disagreeable odor, somewhat suggestive of that of rotten eggs. It is poisonous, even small quantities causing headache, vertigo, nausea, and other bad symptoms. It is soluble in water, about three volumes being taken up at ordinary temperatures. This solution is sometimes used in the laboratory instead of the gas. Hydrogen sulphide is easily decomposed into its elements. In consequence of this instability, it causes a number of changes which the analogous compound water cannot effect. The relations here are similar to those which exist between hydrochloric and hydriodic acids. Hydrochloric acid is very stable, while hydriodic acid breaks down readily into hydrogen and iodine. Chlorine, bromine, and iodine act upon hydrogen sulphide, setting the sulphur free and combining with the hydrogen. Thus, with chlorine the action takes place as represented in the equation



[Does chlorine ever act in a similar way on water? Under what circumstances? (See page 116.) What is the peculiarity of the oxygen given off?]

Most metals when heated in the gas are converted into sulphides. Thus, when it is passed over heated iron this reaction takes place:

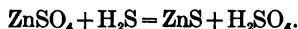


[What takes place when water-vapor is passed over heated iron?]

Many of the sulphides are insoluble in water. Hence, when hydrogen sulphide is passed through solutions containing metals in the form of soluble salts, the insoluble sulphides are thrown down, or *precipitated*.

#### PRECIPITATION OF SULPHIDES BY HYDROGEN SULPHIDE.

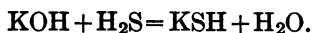
*Experiment 113.*—(tt) Pass hydrogen sulphide through a solution containing a little *lead nitrate*, through another containing a little *zinc sulphate*, and another containing *arsenic* prepared by dissolving a little white arsenic, or arsenic trioxide,  $As_2O_3$ , in dilute hydrochloric acid. In the vessel containing the lead a black precipitate of lead sulphide will be formed; in the one containing the zinc sulphate there will be formed a white precipitate of zinc sulphide; in the one containing the arsenic, a straw-yellow precipitate of arsenic sulphide will be formed. In all these cases the hydrogen of the hydrogen sulphide and the metal of the salt exchange places. For example, in the case of zinc sulphate the reaction takes place thus:



**Chemical Analysis.**—In dealing with chemical substances the first thing we have to determine is their composition, or, in other words, we have to analyze them. For this purpose the properties of the elements and their general conduct towards chemical substances must, of course, be known. To facilitate the process of analysis the mixture to be examined is usually brought into solution and then treated successively with certain substances, the effect being observed in each case. Suppose we had a solution containing most of the metallic elements in the form of salts. If we were to pass through this solution hydrogen sulphide, some of the metals would be precipitated in the form of sulphides,

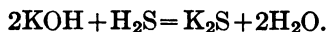
while others would remain in solution, as their sulphides are soluble. We then filter off the precipitate and examine it by other methods, and we could also further examine the solution from which the sulphides were precipitated. By adding to this another reagent which will precipitate some of the metals and leave the others in solution, we can learn still more in regard to the composition of the substance under examination. Hydrogen sulphide is constantly made use of in the laboratory for the purposes of analysis.

**Hydrosulphides.**—When hydrogen sulphide acts upon hydroxides, the action consists in the formation of *hydrosulphides*. In the case of potassium hydroxide the action takes place thus:

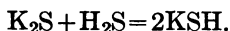


The oxygen and sulphur simply exchange places.

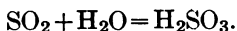
If only half enough hydrogen sulphide is passed into the solution to effect the above change, a sulphide is formed thus:



Or if hydrogen sulphide is allowed to act on potassium sulphide, the product is potassium hydrosulphide:

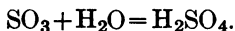


**Compounds of Sulphur with Oxygen and with Hydrogen and Oxygen.**—When sulphur burns in the air it forms the dioxide  $\text{SO}_2$ . Under certain conditions the dioxide combines with more oxygen, forming the trioxide  $\text{SO}_3$ . When sulphur dioxide acts upon water, sulphurous acid is formed:



[What analogy is there between the acid thus formed and carbonic acid?]

When the trioxide combines with water, sulphuric acid is formed:



**Sulphur Dioxide,  $\text{SO}_2$ .**—This compound is formed by burning sulphur in the air or in oxygen. It issues from volcanoes in large quantities. It is best prepared by heating copper with sulphuric acid. The reaction is represented by this equation:



Sulphur dioxide is a colorless gas of an unpleasant, suffocating odor, familiar to every one as that of burning sulphur-matches. Water absorbs it readily. It is easily liquefied by cold.

#### SULPHUR DIOXIDE

*Experiment 114.*—Put about 15 grams copper turnings in a 500-cc. flask; pour 15 to 20 cc. concentrated sulphuric acid upon it. On heating gently, sulphur dioxide will be evolved. The moment the gas begins to come off, lower the flame, and keep it at such a height that the evolution of gas is regular and not too active. Pass some of the gas into a bottle containing water. Fill a vessel by displacement of air. Its specific gravity is 2.26. See whether the gas will burn or support combustion.

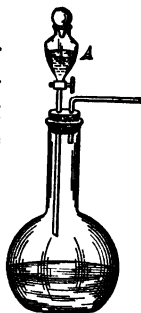
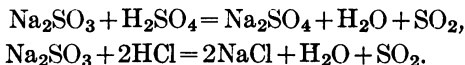


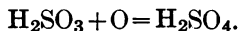
FIG. 48.

*Experiment 115.*—Arrange an apparatus as shown in Fig. 48. *A* is a funnel-tube provided with a stop-cock. In the flask put a solution of acid sodium sulphite,  $\text{HNaSO}_3$ , containing 40 grams of the acid sodium sulphite to 100 ccm. of water; in the funnel, after closing the stop-cock, put ordinary concentrated sulphuric acid. Open the stop-cock very little, so that the sulphuric acid *drops* into the solution below. A regular evolution of sulphur dioxide can thus be maintained.

**Sulphurous Acid,  $\text{H}_2\text{SO}_3$ .**—The solution of sulphur dioxide in water has acid properties, and probably contains the ions of the acid  $\text{H}_2\text{SO}_3$ . By neutralizing the solution with bases, the *sulphites*, or salts of sulphurous acid, are obtained. The sulphites are analogous to the carbonates in composition, and suffer the same decomposition when treated with acids. When a carbonate is treated with an acid, carbon dioxide is given off. So, also, when a sulphite is treated with an acid, sulphur dioxide is given off:



When a solution of sulphur dioxide is allowed to stand in the air in loosely-stoppered bottles, it takes up oxygen, the sulphurous acid being converted into sulphuric acid:



Sulphur dioxide is a good bleaching agent, and is extensively used for the purpose of bleaching wool, silk, straw, paper, etc. In some cases the bleaching is due to the fact that the sulphur dioxide extracts oxygen from the colored substances, forming colorless products. In other cases the action is more complicated.

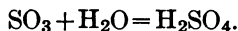
Sulphur dioxide has the power to check fermentation, and is used to preserve liquids that have a tendency to undergo fermentation.

Its principal use is in the manufacture of sulphuric acid. For this purpose it is made in enormous quantities.

#### BLEACHING BY SULPHUR DIOXIDE.

*Experiment 116.*—Burn a little sulphur in a porcelain crucible under a bell-jar. Place over the crucible on a tripod some flowers or a piece of calico. In the atmosphere of sulphur dioxide these will be bleached. Or a bottle containing the colored substance may be filled with sulphur dioxide and then closed.

**Sulphur Trioxide,  $\text{SO}_3$ .**—When sulphur dioxide and oxygen are passed together over certain substances at a somewhat elevated temperature they unite to form sulphur trioxide,  $\text{SO}_3$ . This is a white crystallized solid that melts at  $14.8^\circ$  and boils at  $46^\circ$ . In contact with the air it gives off dense fumes. With water it reacts with great energy to form sulphuric acid:



The substance best adapted to bringing about the combination of sulphur dioxide and oxygen is finely-divided platinum.

#### PREPARATION OF SULPHUR TRIOXIDE.

*Experiment 117.*—Prepare finely divided platinum by moistening some fine asbestos with a solution of platinic chloride and heating to redness in a porcelain crucible. The substance thus obtained is called *platinized asbestos*. Now arrange an apparatus so that both sulphur dioxide and oxygen or air can be passed together through a glass tube, as represented in Fig. 49. First

pass the two gases dried by means of calcium chloride through the empty tube and heat a part of the tube by means of a burner. Is there any evidence of combination? Now stop the currents

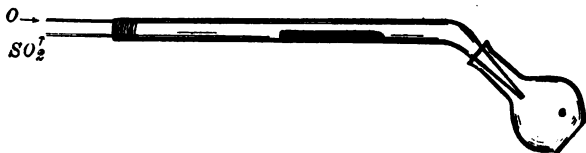
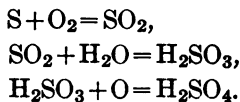


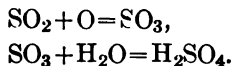
FIG. 49.

of the gases, let the tube cool down, and introduce a small layer of platinized asbestos. Pass the dried gases over the heated asbestos. What takes place?

**Sulphuric Acid,  $\text{H}_2\text{SO}_4$ .**—Sulphuric acid is found in nature in the form of salts, as gypsum, heavy spar, etc. It cannot easily be prepared from its salts, as nitric acid and hydrochloric acids are, and is generally made by oxidizing sulphur dioxide in the presence of water, or, in other words, by oxidizing sulphurous acid. The reactions involved in the manufacture of sulphuric acid are:



Or sulphur dioxide is oxidized to the trioxide  $\text{SO}_3$ , as in Experiment 117, and this then treated with water, in which case the reactions are:



**Manufacture of Sulphuric Acid.**—The oxidation of sulphurous acid as represented in the first series of reactions above cannot readily be effected directly by the action of the oxygen of the air, but an extremely interesting method has been devised by which the oxygen can be transferred from the air to the sulphurous acid. This is accomplished by introducing sulphur dioxide into large chambers together with compounds of nitrogen and oxygen, and steam. The compound of nitrogen and oxygen that plays the chief part in the transformation is the trioxide  $N_2O_3$ . The change is, however, not one of simple direct oxidation, but it involves a number of reactions. Nitric acid is used as the starting-point. This at first reacts with sulphur dioxide and steam, as represented in the equation



The nitrogen trioxide formed combines with sulphur dioxide, oxygen, and water to form a compound which undergoes decomposition with water, yielding sulphuric acid and nitrogen trioxide. This nitrogen trioxide again combines with sulphur dioxide, oxygen, and water. The compound is again decomposed by water and so on. It will be seen, therefore, that the trioxide is not lost, but that it serves the purpose of effecting the oxidation of the sulphur dioxide, and, theoretically, a small quantity of the gas is capable of transforming an infinite quantity of sulphur dioxide into sulphuric acid.

Other reactions besides those mentioned above are undoubtedly involved in the manufacture of sulphuric acid, but, according to the most elaborate researches made in a



factory in operation, those mentioned are the principal ones. Whatever the details may be, the oxidation is effected without serious difficulty, and the waste in nitrogen compounds is now but slight.

In the manufacture of sulphuric acid, sulphur is burned and the sulphur dioxide conducted into large chambers lined with lead. The reason why lead is used is that sulphuric acid acts upon most other available substances.

The above account applies to the method that has long been used in the manufacture of sulphuric acid, and this method is still the principal one in use. Recently, however, the method illustrated in Experiment 117 has come into extensive use especially for the manufacture of the pure, concentrated acid. Various substances are used, or have been recommended, for the purpose of effecting the union of the sulphur dioxide and oxygen. Finely-divided platinum and ferric oxide are the principal ones. This is called the "Contact Process."

**The Product.**—The acid obtained from the leaden chambers contains about 64 per cent of sulphuric acid. It is evaporated in lead pans until it reaches the specific gravity 1.75. As stronger acid acts upon lead, the further evaporation is carried on in platinum, glass, or iron. The strong acid thus obtained is the concentrated sulphuric acid of commerce.

The acid obtained from sulphur trioxide can, of course, be made of any desired concentration.

**Properties of Sulphuric Acid.**—Sulphuric acid is a thick liquid, often somewhat colored by impurities. The pure

acid is colorless. When cooled down it forms crystals. It decomposes the salts of most other acids, setting the acids free, and forming sulphates. We have already had illustrations of this power in the liberation of nitric and hydrochloric acids from their salts by treatment with sulphuric acid.

[Give the equations representing the reactions that take place when common salt and potassium nitrate are treated with sulphuric acid.]

Sulphuric acid unites readily with water, forming compounds with it. The simplest of these is the hydrate  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ . This is a crystallized substance that melts at a low temperature ( $7.5^\circ$ ). A great deal of heat is evolved when sulphuric acid is mixed with water. This fact has been repeatedly illustrated in experiments already performed; and the necessity for precaution in mixing the two liquids has been emphasized. The acid acts upon organic substances containing hydrogen and oxygen, and extracts these elements in the proportion to form water. If a piece of wood is put in the acid it is charred, in consequence of the abstraction of hydrogen and oxygen. [How is wood usually charred in the preparation of charcoal? Is there any analogy between the preparation of charcoal in the ordinary way and by the action of sulphuric acid?] Wounds caused by sulphuric acid are painful and difficult to heal.\*

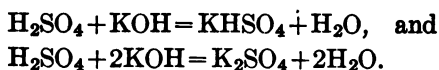
**Uses of Sulphuric Acid.**—Sulphuric acid is one of the most important chemical substances. It is used in enormous

\* A paste made by mixing sodium carbonate and water should quickly be applied to such wounds.

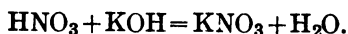
quantities in the manufacture of sodium sulphate, of sodium carbonate, of artificial fertilizers, of nitroglycerin, of glucose, of artificial dyes, etc., and in the refining of petroleum.

The acid is often used in the laboratory for the purpose of drying gases upon which it does not act. [Can it be used for drying ammonia?]

**Monobasic and Dibasic Acids.**—Sulphuric acid differs markedly from nitric and hydrochloric acids in one respect. It has the power to form two different salts with the same metal, in one of which there is relatively twice as much metal as in the other. If to a given quantity of sulphuric acid there is added only half the quantity of caustic potash required to neutralize it, a salt is formed which crystallizes. It has the composition represented by the formula  $\text{KHSO}_4$ . If nitric acid is treated in the same way, only half the acid is acted on, and the product is potassium nitrate,  $\text{KNO}_3$ , the rest of the acid being left unacted upon. In the case of sulphuric acid two reactions are possible, *viz.*:



In the case of nitric acid only one reaction seems to be possible:



Acids which, like sulphuric acid, have the power to form two salts with the same univalent metal are called *dibasic acids*. Acids which, like nitric acid, have the power to form only one salt with the same univalent metal are called

*monobasic acids.* This power is connected with the number of replaceable hydrogen atoms contained in the molecule of the acids. An acid containing two replaceable hydrogen atoms in its molecule is dibasic; one containing one replaceable hydrogen atom in its molecule is monobasic.

**Acid, Neutral, and Normal Salts.**—A dibasic acid yields two classes of salts: (1) those in which all the hydrogen is replaced by metal, and (2) those in which half the hydrogen is replaced by metal. An example of the first class is potassium sulphate,  $K_2SO_4$ ; and an example of the second class is acid potassium sulphate,  $HKSO_4$ .

Salts of the first class that contain no replaceable hydrogen are called *normal salts*. They are generally, though not always, neutral and are sometimes called *neutral salts*.

Salts of the second class are called *acid salts*. Acid salts contain replaceable hydrogen.

**Other Acids containing Sulphur.** — Besides sulphurous and sulphuric acids, sulphur forms several other acids. These cannot be treated of here. Their names and formulas are as follows:

Hyposulphurous acid, $H_2SO_2$ ;	Pyrosulphuric acid, $H_2S_2O_7$ ;
Thiosulphuric acid, $H_2S_2O_3$ ;	Trithionic acid, $H_2S_3O_6$ ;
Dithionic acid, $H_2S_2O_6$ ;	Tetrathionic acid, $H_2S_4O_6$ .

The sodium salt of thiosulphuric acid,  $Na_2S_2O_3$ , commonly called *sodium hyposulphite*, is used in photography. *Pyrosulphuric acid*, or *fuming sulphuric acid*, breaks up into sulphuric acid and sulphur trioxide,  $H_2S_2O_7 = H_2SO_4 + SO_3$ , and is a powerful reagent for some purposes.

**Carbon Bisulphide,  $CS_2$ .**—This compound is formed by bringing sulphur and carbon together at high temperatures. The best method appears to be an electrical one. Sulphur is heated by means of carbon electrodes and the vapor heated to a high temperature rises into a furnace containing charcoal which is also highly heated.

Carbon bisulphide when pure is nearly colorless and has a pleasant odor. It readily becomes impure by standing and then is yellow and has a very disagreeable odor. It boils at  $46^\circ$ , and takes fire easily. It must hence be handled with care. It dissolves sulphur (see Experiments 9, page 12, and 110, page 287) phosphorus, camphor, wax, tar, resins, rubber, and nearly all oils and fats. It is hence used extensively as a solvent. It is also a good disinfectant, germicide, and insecticide, and finds application in agriculture, and in museums and herbariums.

**Selenium and Tellurium and their Compounds.**—These elements are comparatively rarely met with. Tellurium compounds are, to be sure, available in large quantity as a waste-product in the electrolytic refining of copper. In general, the properties of the two elements are very similar to those of sulphur, and they form compounds analogous to the principal compounds of sulphur. They combine with hydrogen, forming gases which have bad odors, somewhat resembling that of hydrogen sulphide. They burn in oxygen, forming oxides,  $SeO_2$  and  $TeO_2$ . Corresponding to these oxides there are acids,  $H_2SeO_3$  and  $H_2TeO_3$ , analogous to sulphurous acid, and  $H_2SeO_4$  and  $H_2TeO_4$ , analogous to sulphuric acid. The compounds with hydrogen are less stable than hydrogen sulphide.

The relation between the atomic weights of the three elements of the sulphur group has already been referred to.

**Points of Resemblance between Oxygen and the Members of the Sulphur Group.**—Between the elements oxygen and sulphur there is but little resemblance, but the compounds of the two elements present many points of analogy. This is seen particularly in the compounds which they form with hydrogen and with the metals. Water and hydrogen sulphide are analogous in composition and in their decompositions. This is also markedly true of the metallic oxides and sulphides; and of the hydroxides and hydrosulphides. On the other hand, oxygen is unique in many respects, and is certainly not nearly as closely related to sulphur as selenium and tellurium are.

## CHAPTER XVII.

### THE NITROGEN GROUP: NITROGEN, PHOSPHORUS ARSENIC, ANTIMONY, AND BISMUTH.

**General.**—Between the element nitrogen and the other elements which are included in this group there is but little resemblance. Nitrogen is a very inactive element under ordinary conditions. Phosphorus, on the other hand, is one of the most active. Nitrogen does not combine directly with oxygen except under the influence of electric sparks. Phosphorus combines with oxygen even at ordinary temperatures, while at the burning-temperature the combination takes place energetically. The elements arsenic and antimony resemble each other in many respects, and are also allied to phosphorus; and antimony and bismuth resemble each other closely. On studying the compounds which all the members of the family form, the fact that they are closely related is clearly recognized.

**Phosphorus P** (At. Wt. 31).—This element occurs in nature in the form of phosphates, or salts of phosphoric acid. The chief of these is calcium phosphate, which is the principal constituent of the minerals *phosphorite* and *apatite* and of the ashes of bones. It occurs also in the form

of organic compounds of phosphorus in the brain and nerve substance of man and animals, in eggs, in albumen, and in plants, especially in the seeds of plants. Phosphorus is also contained in the so-called basic slags from the basic steel processes. These slags are used as fertilizers on account of the phosphate contained in them.

**Preparation.**—It is prepared from bone-ash. This is first treated with sulphuric acid. The acid converts it into a compound, which, when mixed with charcoal and heated, is reduced, yielding free phosphorus. The phosphorus thus obtained is cast into sticks under water, and preserved under water.

The method that is now most commonly used consists in heating an intimate mixture of carbon and a phosphate in an electric furnace. By this method the use of sulphuric acid is avoided.

At the time of the last report available about 3000 tons of phosphorus was manufactured in one year in England and in France and Germany. Quite recently phosphorus has been manufactured to some extent in Sweden.

**Properties.**—It is colorless or slightly yellow and translucent. At ordinary temperatures it can be cut like wax, but it becomes hard and brittle at lower temperatures. It melts at a low temperature ( $44^{\circ}$ ) and boils at  $290^{\circ}$ . Unless carefully protected from the light, its appearance changes. It becomes opaque and darker in color, and finally dark red. This change can be hastened by heating the phosphorus in a sealed tube to a temperature of about  $250^{\circ}$ .

It is insoluble in water, but soluble in carbon bisulphide.



It is very poisonous, the inhalation of the vapor in small quantities causing serious disturbance of the system. The workmen in the factories in which phosphorus is made or used are frequently affected by phosphorus-poisoning. Among the prominent symptoms is a gradual decay of the bones (necrosis).

In contact with the air phosphorus gives off fumes which emit a pale light known as phosphorescence and visible in a dark room. It takes fire when rubbed or cut, and must hence be handled with great care. It should always be cut under water, and never held in the hand, because it takes fire easily, and burns caused by phosphorus are difficult to heal (see page 30). It not only combines with oxygen easily, but with other elements, such as chlorine, bromine, and iodine, the action in each case being accompanied by an evolution of heat and light. The combination of phosphorus with oxygen has already been seen. Its conduct towards iodine can be shown by a very simple experiment.

#### COMBINATION OF PHOSPHORUS AND IODINE.

*Experiment 118.*—Bring together in a porcelain crucible or evaporating-dish a small piece of phosphorus about the size of a pea and about the same quantity of iodine. It will be seen that simple contact is sufficient to cause the two substances to act upon each other. Direct combination takes place, and the action is accompanied by light and heat.

**Red Phosphorus.**—The red substance formed when ordinary phosphorus is exposed to the light, or heated without access of air, is a second variety of phosphorus known as red phosphorus. This differs from ordinary phosphorus

as much as graphite differs from the diamond. Ordinary phosphorus is very active, combining readily with oxygen; it is soluble in carbon bisulphide, and is poisonous. Red phosphorus, on the other hand, is inactive. It does not change in the air, and must be heated to a comparatively high temperature before it will combine with oxygen; it is insoluble in carbon bisulphide, and is not poisonous. Red phosphorus is converted into the ordinary variety by heating it to about  $300^{\circ}$ .

The cause of the great difference in the properties of the two varieties of phosphorus is not known.

There are some other modifications of phosphorus, but they are rarely met with.

**Applications of Phosphorus.**—Phosphorus is used principally in the manufacture of matches, and as a poison for vermin. Various mixtures are used for matches. Nearly all of them contain phosphorus, together with some oxidizing compound, and some neutral substance to act as a medium for holding the constituents together. An example is a mixture consisting of 2 parts phosphorus, 1 part manganese dioxide, 3 parts chalk,  $\frac{1}{8}$  part lampblack, and 5 parts glue. The mixture used for "safety-matches" consists of potassium chlorate, minium, and antimony trisulphide. This will not ignite by simple friction, but will ignite if drawn across a paper on which is a mixture of red phosphorus and antimony pentasulphide. It will also ignite if drawn very quickly across a plate of glass or a sheet of smooth paper.

**Phosphine, Phosphuretted Hydrogen,  $\text{PH}_3$ .**—The chief compound of phosphorus and hydrogen is phosphine,  $\text{PH}_3$ .

It is made by dissolving phosphorus in caustic potash or soda. The reaction which takes place is not altogether simple, and need not be explained at present. The points of chief interest in regard to the substance are: (1) its composition,  $\text{PH}_3$ , which is analogous to that of ammonia,  $\text{NH}_3$ ; (2) its power to combine with some acids as ammonia does, forming unstable phosphonium salts analogous to the ammonium salts; and (3) its power as ordinarily prepared to take fire when brought in contact with the air.

It has a disagreeable odor.

## PHOSPHINE.

*Experiment 119.\*—(T) This experiment requires caution; a careless worker should not be permitted to perform it.—Arrange an apparatus as shown in Fig. 50. In the flask B, which should not*

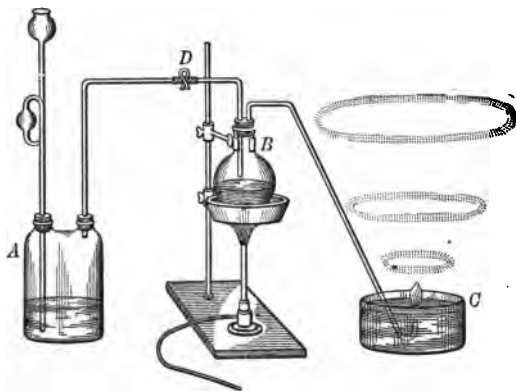


FIG. 50.

be larger than the 100-cc. or 125-cc. size, put about 5 grams caustic potash, dissolved in 10–15 cc. water, and, *after the solution has*

\* It will generally be best to omit Experiments 119 and 120.

become quite cold, add a few small pieces of phosphorus the size of a pea, and push the stopper in tight. Pass hydrogen free from air for some time through the apparatus from the generating-flask *A* until all the air is displaced; then disconnect at *D*, leaving the rubber tube, closed by the pinch-cock, on the tube which enters the flask. Gently heat the contents of the retort, when gradually a gas will be evolved and will escape through the water in *C*. As each bubble comes in contact with the air it takes fire, and the products of combustion arrange themselves in rings which become larger as they rise. They are extremely beautiful, particularly if the air of the room is quiet. Both the phosphorus and the hydrogen combine with oxygen in the act of burning. See Experiment 120. After the required amount of gas has been obtained remove the flame and allow the water to run back into the flask.

**Phosphine itself does not Take Fire Spontaneously.—**

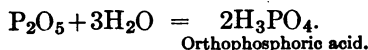
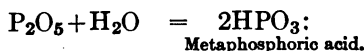
The spontaneous inflammability of phosphine has been found to be due to the presence of a small quantity of another compound of phosphorus and hydrogen which is formed by the action of phosphorus on caustic potash. This is a liquid and has the composition  $P_2H_4$ . It is decomposed by exposure to light, so that phosphine which is thus exposed loses the power to take fire by contact with the air.

**PHOSPHINE NOT SPONTANEOUSLY INFLAMMABLE.**

*Experiment 120.*—(T) Collect a good-sized test-tube full of phosphine by displacement of water, and let it stand over water for a few hours. Now remove the tube from the water and let the gas escape into the air. Does it take fire?

**Compounds of Phosphorus with Oxygen and with Hydrogen and Oxygen.**—The product formed by the direct combination of phosphorus and oxygen under ordinary

circumstances has the composition expressed by the formula  $P_2O_5$ . This combines with water in different proportions, forming two distinct acids, known as *metaphosphoric* and *orthophosphoric acids*.



The formation of metaphosphoric acid takes place at ordinary temperatures, that of orthophosphoric on long standing with water at ordinary temperatures or by boiling with water.

**Orthophosphoric or Ordinary Phosphoric Acid,  $H_3PO_4$ ,** is the principal compound of phosphorus. It is the final product of the action of air and moisture on the element. As has been stated, it occurs in nature as the calcium salt in phosphorite and apatite. This salt is also the chief constituent of bone-ash.

It can be made by treating bone-ash with sulphuric acid, and by oxidizing phosphorus.

It is a solid crystallized substance.

Phosphoric acid has the power of forming three distinct salts with the same metal. It is hence called *tribasic*. With sodium, for example, it forms the three salts  $Na_3PO_4$ ,  $Na_2HPO_4$ , and  $NaH_2PO_4$ . Its normal calcium salt—that is to say, the one in which calcium is substituted for all the three hydrogen atoms—has the formula  $Ca_3(PO_4)_2$ , three bivalent calcium atoms taking the place of six atoms of hydrogen.

[Write the equation expressing the action that takes

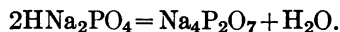
place when sulphuric acid decomposes normal calcium phosphate, forming calcium sulphate and phosphoric acid.]

**Metaphosphoric Acid,  $\text{HPO}_3$ .**—When phosphoric acid is heated to a sufficiently high temperature, it loses hydrogen and oxygen in the form of water and yields *metaphosphoric acid*:

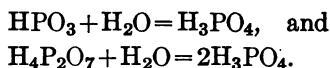


Metaphosphoric acid is the substance that is sold under the name of *glacial phosphoric acid*. It is made by evaporating solutions of phosphoric acid down to dryness and heating the residue.

**Pyrophosphoric Acid,  $\text{H}_4\text{P}_2\text{O}_7$ .**—When a salt like ordinary sodium phosphate,  $\text{HNa}_2\text{PO}_4$ , is heated, it loses water and yields a salt of *pyrophosphoric acid*:



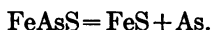
It will thus be seen that ordinary phosphoric acid by losing water yields pyrophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_7$ , and metaphosphoric acid,  $\text{HPO}_3$ . Both of these acids take up water and are reconverted into ordinary phosphoric acid:



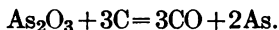
**Phosphorous Acid,  $\text{H}_3\text{PO}_3$ .**—This acid is formed by allowing moist air to act on phosphorus.

**Arsenic, As (At. Wt. 75).**—Arsenic occurs in nature in combination with metals—as, for example, iron, copper, cobalt, nickel, etc.—and in combination with oxygen, in the form of the trioxide  $\text{As}_2\text{O}_3$ .

It is generally obtained by heating arsenical pyrites,  $\text{FeAsS}$ , when the arsenic separates from the iron and sulphur:



It is also made by reducing arsenic trioxide:



It has a metallic lustre. When heated to a high temperature in the air it takes fire, and burns with a bluish flame, giving off fumes which have the odor of garlic and are poisonous.

It combines directly with most elements. In the elementary form it is not poisonous, but when oxidized it becomes so.

**Arsine, Arseniuretted Hydrogen,  $\text{AsH}_3$ .**—This compound is analogous to ammonia and phosphine. It is made by the action of nascent hydrogen [What is nascent hydrogen?] on the compounds of arsenic with oxygen, as when these compounds are brought into a vessel containing zinc and sulphuric acid.

#### ARSINE.

*Experiment 121.\*—The gas formed in this experiment is extremely poisonous. The experiment should be performed only under a good hood having a strong draft to draw off the poisonous gas should any escape.*—Arrange an apparatus as shown in Fig. 50. Put some granulated zinc in the small flask and pour dilute sulphuric acid on it. When the air is all out of the vessel and the hydrogen is lighted, add slowly a little of the solution of arsenic trioxide,  $\text{As}_2\text{O}_3$ ,

\* It will generally be best to omit Experiments 121, 122, 123, 124, 125, 126.

in dilute hydrochloric acid. The appearance of the flame will soon change, becoming paler, with a slightly bluish tint, and giving off white fumes. (See Experiment 122.)

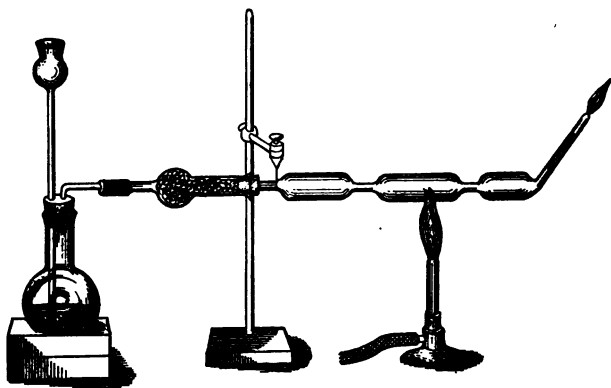


FIG. 51.

**Properties of Arsine.**—Arsine is a colorless gas which is poisonous and has an unpleasant odor. When lighted it burns with a bluish-white flame, forming arsenic trioxide and water. It is very unstable, breaking up into arsenic and hydrogen when heated. When a cold object, as a piece of porcelain, is brought into the flame of burning arsine, the arsenic is deposited in the form of a dark spot. This fact is taken advantage of for the purpose of testing for arsenic in examining the stomach and other viscera in cases of suspected poisoning. The method is known as *Marsh's test*, as it was devised by a chemist by the name of Marsh.



## MARSH'S TEST FOR ARSENIC.

*Experiment 122.*—Into the flame of the burning hydrogen and arsine produced in the last experiment introduce a piece of porcelain, as the bottom of a small porcelain dish or a crucible, and notice the appearance of the spots. Heat, by means of a Bunsen burner, the tube through which the gas is passing, which should be of hard glass. Just in front of the heated place, a thin layer of metallic arsenic, commonly called a *mirror of arsenic*, will be deposited. This deposit is due to the direct decomposition of the arsine into arsenic and hydrogen by heat. [Compare ammonia, phosphine, and arsine with reference to their stability.]

Arsine has no basic properties, differing markedly in this respect from ammonia. Phosphine, as has been stated, has weak basic properties.

**Arsenic Trioxide,  $\text{As}_2\text{O}_3$ .**—When arsenic is burned in the air or in oxygen it forms the trioxide. [Compare with phosphorus in this respect, page 310.] This substance, which is generally called arsenic, is made by heating compounds of arsenic and metals in contact with the air. Under these circumstances, both the metal and the arsenic are oxidized, and the oxide of arsenic, being volatile, passes off and is condensed and collected in large brick chambers.

It is a colorless, amorphous, glassy mass. It is difficultly soluble in water, more easily in hydrochloric acid. It has a weak, disagreeable sweet taste, and is very poisonous. It is probably more frequently used as a poison than any other substance. Minute quantities can be detected by the chemist with absolute certainty.

The oxide is easily reduced by means of carbon.

## REDUCTION OF ARSENIC TRIOXIDE BY CARBON.

*Experiment 123.*—Mix together about equal small quantities of arsenic trioxide and finely-powdered charcoal. Heat the mixture in a small dry tube of hard glass, closed at one end. The arsenic which is set free will be deposited on the walls of the tube in the form of a mirror, like that obtained in Experiment 122.

**Uses.**—Arsenic trioxide (arsenic, white arsenic) is used in making various pigments, for preparing fly and rat poisons, as a preservative for green hides, and in medicine.

**Acids of Arsenic.**—Arsenic forms with oxygen and hydrogen an acid of the formula  $H_3AsO_4$ , known as *arsenic acid*, which is analogous to orthophosphoric acid. When heated, it undergoes changes similar to those referred to in connection with phosphoric acid, the products being *metarsenic acid*,  $HAsO_3$ , and *pyroarsenic acid*,  $H_4As_2O_7$ .

When arsenic trioxide is treated with bases in solution, salts of *arsenious acid*, or the *arsenites*, are formed. The formula of the potassium salt is  $K_3AsO_3$ . The acid  $H_3AsO_3$  differs from arsenic acid,  $H_3AsO_4$ , by one atom of oxygen in the molecule.

**Antimony, Sb (At. Wt. 120).**—This element occurs most frequently in combination with sulphur as the sulphide  $Sb_2S_3$ . It is a silver-white, metallic-looking substance. It melts at  $625^\circ$ . At ordinary temperature it is not changed by contact with the air; but when heated to a sufficiently high temperature in the air it takes fire and burns, forming the white oxide.

**Applications of Antimony.**—Antimony is used as a con-

stituent of several alloys (which see). These will be discussed later on. The value of antimony as a constituent of alloys consists in the fact that it renders them hard. The fact that liquid antimony like water expands on solidifying makes it valuable for type-metal as the expanding metal fills the matrix. Among the soluble alloys of antimony are type-metal, from which type is made, and britania metal. The former consists of lead and antimony, and the latter of tin and antimony. There are a number of other alloys that contain antimony. These will be referred to under the other constituents.

#### BURNING OF ANTIMONY.

*Experiment 124.*—Heat a small piece of antimony on charcoal by means of the blowpipe. Notice the formation of the white coating on the charcoal around the place where the substance burns. What difference is there between the conduct of antimony and arsenic before the blowpipe?

**Stibine, Antimoniuretted Hydrogen,  $\text{SbH}_3$ .**—This compound is made in the same way as arsine.

#### STIBINE.

*Experiment 125.*—The same precautions should be taken in performing this experiment and the following one as in the corresponding experiments with arsenic (see pages 313, 315). Make some stibine, using a solution of tartar emetic in hydrochloric acid.

Its properties are very much like those of arsine. It burns with a similar flame and is decomposed in the same way.

#### ANTIMONY SPOT.

*Experiment 126.*—Introduce a piece of porcelain into the flame and notice the deposit or antimony spot. It is darker and more

smoky than the arsenic spot. There are other differences in properties by which they can be distinguished from each other with absolute certainty.

**Acids of Antimony.**—Antimony forms acids resembling phosphoric, metaphosphoric, and pyrophosphoric acids.

**Antimony as a Base-forming Element.**—Antimony not only forms acids with hydrogen and oxygen, but it also forms bases. These bases neutralize acids and form salts in which antimony takes the place of the hydrogen of the acids. Some of these salts are rather complicated in composition, and it would lead too far to discuss them here. It is sufficient for the present to recognize the important fact that one and the same element has the power to form acids and bases.

Antimony, however, is not the only element thus far studied which has this double power. The compounds of nitrogen with hydrogen and oxygen have, in general, acid properties, but ammonia has strongly basic properties. It will be seen, therefore, that when nitrogen is combined with hydrogen the product has basic properties, while when combined with hydrogen and oxygen in forms in which the oxygen is in excess the products are acids. The same is true to some extent of phosphorus.

At the same time, neither the element nitrogen nor the element phosphorus itself has the power to take the place of the hydrogen of acids, and this power antimony has.

**Bismuth, Bi** (At. Wt. 208.5).—Bismuth is not abundant nor widely distributed in nature. It occurs for the most part native, or uncombined, in veins of granite or clay slate. It occurs also as the oxide  $\text{Bi}_2\text{O}_3$ , and as the sulphide  $\text{Bi}_2\text{S}_3$ .

It is a hard, brittle, reddish-white substance with a metallic lustre. It looks very much like antimony, but is distinguished from it by its reddish tint. At ordinary temperature it remains unchanged in the air, but when heated to redness it burns with a bluish flame, forming the yellow oxide  $\text{Bi}_2\text{O}_3$ .

#### BURNING OF BISMUTH.

*Experiment 127.*—Heat a small piece of bismuth on charcoal by means of the blowpipe. Compare the result with those obtained with antimony and with arsenic.

Some bismuth is used in the preparation of alloys that are easily fusible, as, for example, Newton's metal, which contains bismuth, lead, and tin; Rose's metal, which consists of the same constituents in slightly different proportions; and Wood's metal, which consists of bismuth, lead, tin, and cadmium.

Bismuth possesses in a still greater degree than antimony the property of expansion on passing from the liquid to the solid state. This in connection with the low melting-point of its alloys renders it valuable for making plates for printing drawings and pictures.

**Salts of Bismuth.**—Bismuth forms two classes of salts, known as *bismuth* and *bismuthyl salts*. In the former the bismuth acts as a trivalent metal taking the place of three atoms of hydrogen as in the nitrate  $\text{Bi}(\text{NO}_3)_3$ . In the bismuthyl salts the group bismuthyl,  $\text{BiO}$ , takes the place of one atom of hydrogen, as in bismuthyl nitrate,  $\text{BiO}(\text{NO}_3)$ . Antimony forms salts similar to both these classes.

**Bismuth Nitrates.**—When bismuth is dissolved in nitric acid and the solution evaporated to dryness the salt  $\text{Bi}(\text{NO}_3)_3 + 10\text{H}_2\text{O}$  is obtained. This salt is decomposed by water and also when heated, forming *basic nitrates of bismuth*. These differ in composition according to the method of preparation, but all are formed by incomplete neutralization of the base  $\text{Bi}(\text{OH})_3$ . The basic nitrate of bismuth, or the *subnitrate*, as it is called in pharmacy, is much used in medicine as a remedy in dysentery and cholera. It is also used as a cosmetic.

**General Remarks on the Characteristics of the Nitrogen Group.**—The resemblance between nitrogen and phosphorus is seen especially in the compounds ammonia and phosphine. Between the oxides of nitrogen and of phosphorus the resemblance is not striking. There are two oxides of nitrogen,—the trioxide,  $\text{N}_2\text{O}_3$ , and the pentoxide,  $\text{N}_2\text{O}_5$ ,—which in composition correspond to the two oxides of phosphorus,  $\text{P}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$ . But while the pentoxide of phosphorus is the most common oxide of this element, the pentoxide of nitrogen is obtained with greater difficulty than any of the other oxides of nitrogen. There are no compounds of phosphorus analogous to the three principal oxides of nitrogen,—nitrous oxide,  $\text{N}_2\text{O}$ ; nitric oxide,  $\text{NO}$ ; and nitrogen peroxide,  $\text{NO}_2$ . There is no acid of phosphorus corresponding to nitrous acid,  $\text{HNO}_2$ , and there are no compounds of nitrogen analogous to phosphoric acid,  $\text{H}_3\text{PO}_4$ , and pyrophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_7$ . Nitric acid,  $\text{HNO}_3$ , and metaphosphoric acid,  $\text{HPO}_3$ , have analogous compositions.

The resemblance between phosphorus, arsenic, and anti-

mony is much more striking than that between nitrogen and phosphorus. This resemblance has already been noted in the acids formed by the three elements, and in their hydrogen compounds,  $\text{PH}_3$ ,  $\text{AsH}_3$ , and  $\text{SbH}_3$ , all of which are analogous to ammonia. The same resemblance is seen in their oxides,  $\text{P}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{As}_2\text{O}_3$ ,  $\text{As}_2\text{O}_5$ , and  $\text{Sb}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_5$ . Their compounds with chlorine and the other members of the chlorine group are also strikingly similar. Antimony and bismuth closely resemble each other in some respects. The latter forms two oxides,  $\text{Bi}_2\text{O}_3$  and  $\text{Bi}_2\text{O}_5$ , and forms salts in the same way that antimony does, but the element has very weak acid properties. The elements of the nitrogen group are *trivalent* in some compounds, as in  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$ ,  $\text{PCl}_3$ ,  $\text{AsCl}_3$ , etc.; and *quivalent* in others, as in  $\text{NH}_4\text{Cl}$ , in which the nitrogen is believed to hold in combination four atoms of hydrogen and one atom of chlorine; in  $\text{PCl}_5$ , etc., etc.

The atomic weights are  $\text{N}=14$ ;  $\text{P}=31$ ;  $\text{As}=75$ ;  $\text{Sb}=120$ ;  $\text{Bi}=208.5$ . These figures do not all bear simple relations to one another, but between the atomic weights of phosphorus, arsenic, and antimony there exists a relation similar to that already noticed between the atomic weights of chlorine, bromine, and iodine, and sulphur, selenium, and tellurium. Thus,  $\text{P}=31$ ,  $\text{Sb}=120$ , and  $\text{As}=75$ :

$$\frac{31+120}{2}=75.5.$$

Again, between the atomic weights of phosphorus, antimony, and bismuth a similar relation exists. Thus,  $\text{P}=31$ ,  $\text{Sb}=120$ ,  $\text{Bi}=208.5$ :

$$\frac{31 + 208.5}{2} = 119.75.$$

**Boron, B** (At. Wt. 11). — Boron may conveniently be studied in connection with the nitrogen group, as some of its properties suggest those of the members of the group. At the same time, it presents peculiarities which distinguish it from these elements. Boron occurs in nature in the form of boric acid, or as salts of this acid, especially the sodium salt, or *borax*. Boron is prepared by treating the oxide,  $B_2O_3$ , at a very high temperature with sodium or aluminium. Under proper conditions it is obtained in the form of crystals which are almost as hard as diamonds.

At a red heat uncrystallized boron combines with nitrogen very readily. The crystallized variety can be heated to a high temperature in the air without changing. These properties distinguish boron from the members of the nitrogen family, all of which, with the exception of nitrogen, combine with oxygen. Boron combines with chlorine, forming the chloride  $BCl_3$ , analogous to the chlorides of phosphorus and arsenic,  $PCl_3$  and  $AsCl_3$ .

**Boric Acid,  $H_3BO_3$ .** — The chief compound of boron is boric acid. It occurs in nature in large quantities, issuing from the earth with water-vapor in some localities, particularly in Tuscany. The jets of steam charged with boric acid, which are called *suffioni*, are conducted into tanks of water, in which the acid condenses. The solution is evaporated by means of the heat of the natural steam-jets, and finally the acid crystallizes out. The acid is also obtained from a natural magnesium salt called *boracite*, from *borax*, which is a sodium salt found in Asia, and in



Nevada and California in the United States, and from colemanite and borocalcite, calcium salts found in California and South America.

Most of the boric acid obtained from Tuscany is used in the manufacture of borax, a salt that finds extensive application.

The most important source of boric acid is colemanite, which occurs in California. About 2500 tons are mined monthly.

When heated to 100° boric acid loses water and is converted into *metaboric acid*,  $\text{HBO}_2$ :



[What is the analogous change of phosphoric acid?]

The acid thus obtained is analogous to nitrous acid in composition.

When heated higher, a larger proportion of water is given off, and an acid of the formula  $\text{H}_2\text{B}_4\text{O}_7$ , or *tetraboric acid*, is left behind. This is the form of boric acid from which borax is derived. The formula of borax is  $\text{Na}_2\text{B}_4\text{O}_7 + 10\text{H}_2\text{O}$ . The relation between tetraboric acid and normal boric acid is shown by the equation



Heated to a still higher temperature, boric acid loses all its hydrogen in the form of water, and *boron trioxide*, or *boric anhydride*,  $\text{B}_2\text{O}_3$ , is left behind.

When a solution of borax is treated with sulphuric acid, boric acid is set free, and crystallizes out if the solution is concentrated enough.

## BORIC ACID FROM BORAX.

*Experiment 128.*—Make a hot solution of 30 grams crystallized borax in 120 cc. water. Add *slowly* 10 grams concentrated sulphuric acid. On cooling, the boric acid will crystallize out. [What evidence have you that the substance which crystallizes out of the solution is not borax?] Try the solubility in alcohol of specimens of each. [Is there any difference?] Treat a few crystals of borax with about 10 cc. alcohol; pour off the alcohol and set fire to it. Treat a few crystals of boric acid in the same way. [What difference do you observe?]

**Boric Anhydride**,  $B_2O_3$ , when heated, melts and forms a transparent substance resembling glass. This has the power to dissolve many substances which ordinary solvents will not dissolve, and some of the solutions thus formed are colored. This fact is taken advantage of in the laboratory for the purpose of detecting the presence of those substances which form such colored solutions. The method of work consists in melting a little boric acid or borax in a loop of platinum wire, and then bringing a minute particle of the substance to be examined in contact with the bead thus formed. When heated before the blowpipe it will generally dissolve. By holding the bead in the oxidizing flame of the blowpipe the substance in solution may be oxidized, and by holding it in the reducing flame it may be reduced. Changes of color may thus be produced which will aid us in determining what substance we have to deal with. This method is valuable for the purposes of analysis.

When an alcoholic solution of boric acid is lighted, it burns with a green flame. The salts of boric acid do not color the alcohol flame. [What evidence have you had of the truth of this statement?]

Boron is trivalent in most of its compounds, as in the chloride,  $BCl_3$ .

## CHAPTER XVIII.

### THE CARBON GROUP: CARBON AND SILICON.

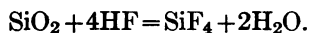
#### TITANIUM—ZIRCONIUM—CERIUM—THORIUM.

**Silicon, Si (At. Wt. 28).**—We have already learned how important a part carbon plays in living things. It is interesting to note that silicon, which in some respects resembles carbon from a chemical point of view, is one of the most important constituents of the mineral or inorganic parts of the earth. It occurs chiefly in the form of the oxide,  $\text{SiO}_2$ , commonly called silica, or silicon dioxide; and in combination with oxygen and several of the common metals, particularly sodium, potassium, aluminium, and calcium, in the form of silicates. Next to oxygen, silicon is the most abundant element in nature. There are extensive mountain-ranges consisting almost entirely of silicon dioxide,  $\text{SiO}_2$ , in the form known as *quartz* or *quartzite*. Other ranges are made up of silicates, which are compounds formed by a combination of silicon dioxide and bases. The clay of valleys, river-beds, etc., also contains silicon in large quantity, while the sand found so abundantly at the seashore is mostly silicon dioxide,  $\text{SiO}_2$ .

Silicon is never found in the free state, and it is difficult to decompose the oxide,  $\text{SiO}_2$ , in such a way as to get the

element, though it can be accomplished by heating the oxide with potassium or magnesium. Under proper conditions silicon can be obtained in the form of crystals that have a gray color and are harder than glass. It is not acted upon by the strongest acids, nor when heated in a current of oxygen.

With hydrogen, silicon forms a gaseous compound of the formula  $\text{SiH}_4$ ; it combines with chlorine, forming  $\text{SiCl}_4$ , and with fluorine, forming  $\text{SiF}_4$ . The fluoride has already been referred to in connection with the action of hydrofluoric acid on silicates. It has been seen that hydrofluoric acid dissolves silicates—as, for example, glass—in consequence of the action of the acid on silicon dioxide. The reaction is represented thus:



The silicon fluoride passes off in the form of gas.

**Silicides** are compounds of silicon with other elements, as, for example, with carbon. These two elements combine forming an interesting compound, *carbon silicide*,  $\text{CSi}$ , which is manufactured on the large scale under the name of *carborundum*. It is made by heating a mixture of quartz sand, coke, and common salt in the electric furnace. It is a very stable substance, and is extremely hard, so that it is used as a substitute for emery.

**Silicic Acid.**—There are several varieties of silicic acid, all of which are, however, derived from an acid of the formula  $\text{H}_4\text{SiO}_4$ , or normal silicic acid. When this is set free

from its salts, it loses water, and is changed to ordinary silicic acid,  $\text{H}_2\text{SiO}_3$ :



When heated, this second form of silicic acid is converted into the dioxide,  $\text{SiO}_2$ :



Most of the ordinary silicates are derived from the acid of the formula  $\text{H}_2\text{SiO}_3$ . [What is the formula of carbonic acid? Under what circumstances does carbonic acid break down into carbon dioxide and water?] Other silicic acids are obtained by heating ordinary silicic acid. Thus, under the proper conditions, an acid of the formula  $\text{H}_2\text{Si}_2\text{O}_5$ , and one of the formula  $\text{H}_4\text{Si}_3\text{O}_8$ , are obtained:



These are called *polysilicic acids*. Some of these are found in nature. Opal is the best-known example.

**Silicon Dioxide, Silicic Anhydride,  $\text{SiO}_2$ .**—As already stated, this substance occurs very abundantly in nature and in many different forms. *Quartz*, or *rock crystal*, is pure crystallized silicon dioxide; *quartzite* is a coarser-grained substance made up of small crystals of quartz, usually colored. *Agate*, *amethyst*, and *carnelian* are varieties of quartz colored by foreign substances.

Silicon dioxide is insoluble in water and acids. It is soluble in hydrofluoric acid, as has been stated.

**Uses.**—Plants take up silicon dioxide from the soil, and this being deposited in various parts of their tissues gives them the necessary firmness. Straw, for example, is rich in silicon dioxide. Horsetail, a plant of the genus *Equisetum*, is so rich in finely divided silicon dioxide that it is used for polishing. There are great natural deposits of finely divided silicon dioxide known as *infusorial earth*. This consists of the remains of diatoms. And finally silicon dioxide is found in hair, in feathers, and in egg albumen. Silicon dioxide finds extensive application in the manufacture of mortar, glass, and porcelain. Ordinary glass is a silicate of calcium and potassium or sodium, made by melting together sand and the carbonates of the metals mentioned.

**Quartz.**—Silicon dioxide expands only one-twelfth as much as the best glass when heated. For this reason flasks and tubes are now made of fused silicon dioxide under the name quartz glass. Such flasks can be heated red hot and plunged into cold water or liquid air without injury, and can be heated to  $1700^{\circ}$ , without softening. The necessarily high price of objects of quartz glass prevents its general substitution for glass for general laboratory use.

**Comparison of Carbon and Silicon.**—The two principal elements of this family resemble each other in the composition of some of their simplest compounds, as carbon dioxide,  $\text{CO}_2$ , and silicon dioxide,  $\text{SiO}_2$ ; carbonic acid,  $\text{H}_2\text{CO}_3$ , and silicic acid,  $\text{H}_2\text{SiO}_3$ ; marsh-gas,  $\text{CH}_4$ , and silicon hydride,  $\text{SiH}_4$ ; carbon tetrachloride,  $\text{CCl}_4$ , and silicon tetrachloride,  $\text{SiCl}_4$ . On the other hand, they present

marked points of difference. Each yields a large number of derivatives, but the derivatives of carbon bear to the element relations entirely different from those which the derivatives of silicon bear to this element. The compounds of carbon can all be shown to be derived from the hydrocarbons; that is to say, they may be regarded as formed from the hydrocarbons by comparatively simple changes, while most of the compounds containing silicon are derivatives of silicic acid.

**Rare Elements of this Group.**—The rare elements *titanium*, *zirconium*, *cerium*, and *thorium* resemble silicon in their chemical conduct. They form oxides of the formulas  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{CeO}_2$ , and  $\text{ThO}_2$ , which are analogous to silicon dioxide. Titanium occurs in nature principally as the dioxide, and forms the three minerals rutile, brookite, and anatase. Zirconium occurs in nature as zircon, which is a silicate of the formula  $\text{ZrSiO}_4$ .

**Thorium Dioxide,  $\text{ThO}_2$ .**—This occurs in nature as the mineral thorite, but is obtained commercially from the mineral monazite which contain about 5 per cent thorium.

*Welsbach mantles* are made by dipping a cylinder of cotton web in a solution of a mixture of thorium and cerium nitrates. When the cotton is burned away a web of thorium and cerium oxides remains which becomes incandescent and yields a strong light when heated with a comparatively small Bunsen flame. Mantles containing 99 per cent thorium oxide and 1 per cent cerium oxide are said to give the best light.

## CHAPTER XIX.

### BASE-FORMING ELEMENTS.—GENERAL CONSIDERATIONS.

**Introductory.** The compounds of the base-forming elements with hydrogen and oxygen are bases, or, in other words, have the power to neutralize acids and form salts. But the distinction between acid-forming and base-forming elements is not a sharp one, for the reason that there are some elements that occupy an intermediate position, forming both acids and bases. One example of this kind already studied is antimony. The reason why it is regarded as a member of the nitrogen group is that it is unquestionably closely related to arsenic, which is an acid-forming element.

**Order in which the Base-forming Elements will be Taken up.**—In studying the base-forming elements, it appears best to begin with those which have the most strongly marked character. These are members of Group I, as shown in the table page 264. It further appears best to adhere as closely as possible to the arrangement in the periodic system. Accordingly the following order will be observed in the presentation of the elements yet to be studied:

1. The *Potassium Group*, consisting of lithium, sodium, potassium, rubidium, and cæsium.



2. The *Calcium Group*, consisting of glucinum, calcium, barium, and strontium.

3. The *Magnesium Group*, consisting of magnesium, zinc, and cadmium.

4. The *Silver Group*, consisting of silver, copper and mercury.

5. The *Aluminium Group*, of which aluminium is the only well-known member. Allied to it are the rare elements gallium, indium, thallium, scandium, yttrium, lanthanum, and ytterbium.

6. The *Lead Group*, consisting of germanium, tin, and lead.

7. The *Chromium Group*, consisting of chromium, molybdenum, and tungsten. The members of this group resemble the members of the sulphur group in some respects, as will be pointed out under chromium.

8. The *Manganese Group*, of which manganese is the only representative. There are some points of resemblance between manganese and the members of the chlorine group.

9. The *Iron Group*, consisting of iron, cobalt, and nickel.

10. The *Palladium Group*, consisting of palladium, ruthenium, and rhodium.

11. The *Platinum Group*, consisting of osmium, iridium, platinum, and gold.

It will be seen at once that there are many more base forming than acid-forming elements. In order to get a general knowledge of the principles of chemistry, however, it is not necessary to study all these elements. The chemist must, of course, familiarize himself to some extent with all of them, and those who continue the study of chemistry hereafter will have abundant opportunity to study them

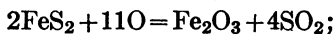
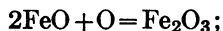
in detail. For the present it will be best to confine attention to a few of the representative elements included in the above list. A knowledge of these will make it possible to study the others without serious difficulty.

**Metallic Properties.**—It has long been customary to divide the chemical elements into two classes,—the *metals* and the *non-metals*. This classification was originally based upon differences in the physical properties of the elements, the name metal being applied to those elements which have a metallic lustre, are opaque, and are good conductors of heat and electricity. All those elements which do not have these properties were called non-metals. Gradually the name metal came to signify an element which has the power to take the place of the hydrogen of acids and form salts, and the name non-metal to signify an element which has not this power. This classification, as will be seen, is about the same as that made use of in this book. It thus appears that, in general, elements that have similar physical properties have also similar chemical properties.

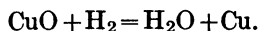
**Occurrence of the Metals.**—One of the first questions that suggests itself in connection with each element is, In what forms of combination does it occur in nature? The chemical elements and compounds that occur ready-formed in nature are called *minerals*, and the minerals and mixtures of minerals from which the metals are extracted for practical purposes are called *ores*. The most common ores are oxides and sulphides. Examples of these are the ores of iron, tin, copper, lead, and zinc. The carbonates also occur in large quantity in nature, and are used for the pur-

pose of preparing some of the metals. The carbonate of zinc, for example, is a valuable ore of zinc.

**Extraction of Metals from their Ores.**—The detailed study of the methods used in the extraction of the metals from their ores is the object of *metallurgy*. Besides the methods used on the large scale, there are others which are only used in the laboratory. The most common method of extracting metals from their ores is that used in the case of iron, which consists in heating the oxides with charcoal or coke. If the ores used are not oxides they must first be converted into oxides before this method is applicable. This can generally be accomplished by heating the ores in contact with the air. Under these circumstances the natural carbonates, sulphides, and hydroxides are converted into oxides. This is called roasting. The changes are illustrated by the following equations:



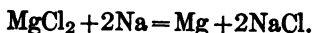
A second method consists in reducing the oxide by heating it in a current of hydrogen. This has been illustrated in the action of hydrogen upon copper oxide, when the following reaction takes place:



The method is efficient for many oxides, but is expensive and is not used on the large scale.

Another method of extraction consists in treating the

chloride of a metal with sodium. This is illustrated in the preparation of magnesium:



Such a method is employed only in case it is impossible or extremely difficult to reduce the oxide.

A number of the metals are obtained by the aid of a powerful electric current. The preparation of aluminium is a good example of this. Metals obtained from their salts by electrolysis are generally pure.

**The Properties of the Metals.**—As we shall find, the metals differ very markedly from one another. Some are light, floating on water, as potassium, sodium, etc.; some are extremely heavy, as lead, platinum, etc. Some combine with oxygen with great energy; others form very unstable compounds with oxygen. Some form strong bases; others form weak bases. In general those elements which are lightest, or which have the lowest specific gravity, are the most active chemically, while those which have the highest specific gravity are the least active. Among the former are lithium, sodium, and potassium; among the latter are lead, gold, and platinum.

**Compounds of the Metals.**—The compounds of the metals may be conveniently classified as:

- a. Compounds with fluorine, chlorine, bromine, and iodine; or the *fluorides*, *chlorides*, *bromides*, and *iodides*.
- b. Compounds with oxygen, and with oxygen and hydrogen; or the *oxides* and *hydroxides*.
- c. Compounds with sulphur, and with sulphur and hydrogen; or the *sulphides* and *hydrosulphides*.

d. Compounds with nitrogen and with the acids of nitrogen; or the *nitrides*, *nitrates*, and *nitrites*.

e. Compounds with the acids of chlorine, bromine, and iodine; or the *chlorates*, *bromates*, *iodates*, *hypochlorites*, etc.

f. Compounds with the acids of sulphur; or the *sulphates*, *sulphites*, *hyposulphites*, etc.

g. Compounds with carbon and with carbonic acid; or the *carbides* and the *carbonates*.

h. Compounds with the acids of phosphorus, arsenic, and antimony; or the *phosphates*, *arsenates*, etc.

i. Compounds with silicic acid; or the *silicates*.

j. Compounds with boric acid; or the *borates*.

Of the large number of compounds belonging to the classes above referred to, only a comparatively small number will be treated of in this book. It is more important to become acquainted with the general methods of preparation and the general properties of these compounds than to learn details concerning many individual members of each class. Only those compounds will be treated of which illustrate general principles, or which, owing to some application, happen to be of special interest.

The acids of which the salts are derivatives are already known to us, and in dealing with acids frequent reference has been made to the methods of making the salts, and to some of their most important properties. It will be well, before taking up the metals systematically, to discuss briefly the general methods of preparation and the general properties of the different classes of metallic compounds. It must be borne in mind, however, that the only way to become familiar with these substances and their relations is by working with them in the laboratory.

## INTRODUCTION TO CHEMISTRY.

**chlorides.**—The chlorides, as well as the fluorides, bromides, and iodides, may be regarded as the salts of hydrochloric, hydrofluoric, hydrobromic, and hydriodic acids, or simply as compounds of the metals with the members of the chlorine group. The most important of these compounds are the chlorides, and these well illustrate the conduct of the others.

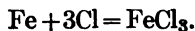
The chlorides are made by treating the metals with hydrochloric acid or chlorine; by treating an oxide or a hydroxide with hydrochloric acid; by treating an oxide with chlorine and a reducing agent, like carbon; by treating a salt of a volatile acid, a carbonate for example, with hydrochloric acid; by treating a salt of an insoluble acid with hydrochloric acid; by adding hydrochloric acid or a soluble chloride to a solution containing a metal with which chlorine forms an insoluble compound; and by adding to a solution of a chloride a salt the acid of which forms with the metal of the chloride an insoluble salt, while the metal contained in it forms with chlorine a soluble chloride.

Only two of the above methods are peculiar to chlorides. These are the treatment of the metals with chlorine, and the treatment of oxides with chlorine and a reducing agent. The others involve principles which are also involved in the preparation of all salts, and they may therefore be treated of in a general way.

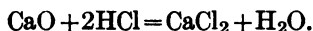
**EXAMPLES.**—Zinc chloride is formed by treating zinc with hydrochloric acid.

[Write the equation.]

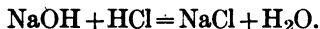
Ferric chloride is formed by treating iron with chlorine:



Calcium chloride is formed by treating lime or calcium oxide,  $\text{CaO}$ , with hydrochloric acid:



Sodium chloride is formed by treating sodium hydroxide, or caustic soda,  $\text{NaOH}$ , with hydrochloric acid:



[What takes place when caustic soda or caustic potash is treated with chlorine (see page 121).]

Calcium chloride is formed when calcium carbonate,  $\text{CaCO}_3$ , is treated with hydrochloric acid:

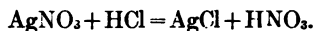


Silver chloride is precipitated when hydrochloric acid or a soluble chloride is added to a solution containing a silver salt.

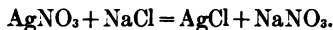
#### SILVER CHLORIDE FORMED BY PRECIPITATION.

*Experiment 129.*— Dissolve a small crystal of silver nitrate in pure water. Add to a small quantity of this solution in a test-tube a few drops of dilute hydrochloric acid. The white substance thus precipitated is silver chloride,  $\text{AgCl}$ . To another small portion of the solution add a few drops of a dilute solution of common salt, or sodium chloride,  $\text{NaCl}$ . The white substance produced in this case is also silver chloride. Add ammonia to each tube. If sufficient is added the precipitates will dissolve. On adding enough hydrochloric acid to these solutions to combine with all the ammonia, the silver chloride is again thrown down. On standing exposed to the light both precipitates change color, becoming finally dark violet. The reactions involved in the above

experiments are these: In the first place, when hydrochloric acid is added to silver nitrate this reaction takes place:



When sodium chloride is added this reaction takes place:



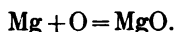
In the first reaction nitric acid is set free; in the second, the sodium and silver exchange places. In addition to the insoluble silver chloride, the soluble salt, sodium nitrate, is formed at the same time. On adding ammonia the silver chloride forms with it a compound which is soluble in water; and, on adding an acid, the ammonia combines with this, leaving the silver chloride uncombined and therefore insoluble.

**General Properties of the Chlorides.**—Most of the chlorides of the metals are soluble in water without decomposition, though many of them are decomposed when heated to a sufficiently high temperature with water. Silver chloride,  $\text{AgCl}$ , and mercurous chloride,  $\text{HgCl}$ , are insoluble in water. Lead chloride,  $\text{PbCl}_2$ , is difficultly soluble in water. If, therefore, on adding hydrochloric acid or a soluble chloride to a solution a precipitate is formed, the conclusion is generally justified that one or more of the three metals—silver, lead, or mercury—is present. By taking into account the differences between these chlorides, it is not difficult to decide of which of them a precipitate consists.

**Oxides.**—These occur very generally in nature, and are among the most common ores of some of the important metals. The oxides of iron, tin, manganese, etc., are all found in nature. They can be made by oxidizing the metals, by heating nitrates and carbonates, and by heating hydroxides.



EXAMPLES.—When magnesium is burned (see Experiment 14, page 16) it is converted into magnesium oxide:



When lead nitrate is heated it gives off oxygen and an oxide of nitrogen and leaves behind lead oxide:



When calcium carbonate is heated it gives off carbon dioxide and leaves behind calcium oxide,  $\text{CaO}$ :

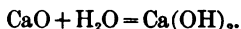


**Hydroxides.**—The hydroxides are formed by treating oxides with water, and by decomposing salts by adding soluble hydroxides.

EXAMPLES.—When calcium oxide or lime is treated with water it is converted into the hydroxide  $\text{Ca}(\text{OH})_2$ , or slaked lime.

#### SLAKING OF LIME.

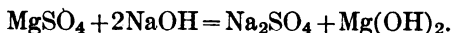
*Experiment 130.*—Moisten some pieces of freshly-burned lime with hot water. The action which takes place is represented by the equation



The process is known as slaking. On the large scale and with freshly-burned lime the reaction takes place with cold water.

Most of the hydroxides of the metals are insoluble in water. If a soluble hydroxide is added to a solution containing a metal whose hydroxide is insoluble, the latter is

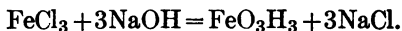
precipitated. Thus, if a solution of sodium hydroxide is added to a solution of a magnesium salt, magnesium hydroxide is precipitated:



#### PRECIPITATION OF MAGNESIUM HYDROXIDE.

*Experiment 131.*—To a small quantity of a dilute solution of magnesium sulphate add a little of a dilute solution of caustic soda. The white precipitate is magnesium hydroxide. [Would you expect this precipitate to be soluble in sulphuric acid? in hydrochloric acid? in nitric acid?] The answers follow from these considerations: When acids act upon hydroxides, salts are formed; magnesium sulphate is soluble, as is shown by the fact that we started with a solution of this salt; the only insoluble chlorides are those of silver, lead, and mercury; all nitrates are soluble.

When a solution of an iron salt is treated with sodium hydroxide a precipitate of iron hydroxide is formed:

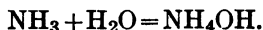


#### PRECIPITATION OF FERRIC HYDROXIDE.

*Experiment 132.*—To a dilute solution of that chloride of iron which is known as ferric chloride add caustic soda. The reddish precipitate formed is ferric hydroxide. [From the general statements made above, would you expect this precipitate to be soluble in sulphuric acid? in hydrochloric acid? in nitric acid? Try each.]

Only the hydroxides of the members of the potassium family and of the calcium family are soluble in water. The hydroxides of sodium and potassium and certain other elements are called *alkalies*. The solution of ammonia in

water acts like a soluble hydroxide and probably contains the ions of ammonium hydroxide,  $\text{NH}_4\text{OH}$ , formed by the action of water on ammonia:



When any one of the soluble hydroxides is added to a salt containing a metal that does not belong to the potassium or calcium family, an insoluble compound is thrown down.

[Test this by trying such salts as may be available. Note the results in each case. Is an insoluble compound formed? What is its general appearance?]

**Decomposition of Salts by Acids and by Bases.** — The decomposition of salts by the addition of hydroxides is in some respects analogous to the decomposition of salts by the addition of strong acids.

When an acid is added to a salt there are three cases which may present themselves:

1. The acid from which the salt is derived may be volatile or may break down, yielding a volatile product.

In this case decomposition takes place, and the volatile acid is given off. This is illustrated by the liberation of hydrochloric and nitric acids from chlorides and nitrates on the addition of sulphuric acid, and of carbon dioxide from carbonates on the addition of other acids.

[Write the equations representing the reactions which take place when sulphuric acid acts upon potassium chloride, calcium chloride, sodium nitrate, calcium nitrate; when hydrochloric acid acts upon sodium carbonate, calcium carbonate.]

2. The acid from which the salt is derived may be insoluble or difficulty soluble in water, and not volatile.

In this case, if the salt is in solution, decomposition takes place, and the insoluble or difficulty soluble acid is precipitated. This is illustrated by the liberation of boric acid from borax by the addition of sulphuric acid; and by the liberation of silicic acid by the addition of hydrochloric or sulphuric acid to a soluble silicate.

3. The acid from which the salt is derived may be soluble and not volatile under the existing conditions.

In this case, if the substances are in solution, apparently no change takes place. Thus, when nitric acid is added to sodium chloride in solution no striking change takes place, no gas is given off, no precipitate is formed. It is extremely difficult to determine what does take place under these circumstances. A study of such cases as this is of great importance to chemistry, but cannot be undertaken at this stage.

Now, to return to the action of hydroxides upon salts; when a soluble base acts upon a salt, three cases may present themselves

1. The base from which the salt is derived may be volatile or may break down, yielding a volatile product.

In this case decomposition takes place and the volatile base is given off. This is not a common case except among the compounds of carbon. The one illustration which we have had is the decomposition of ammonium salts by calcium hydroxide and by sodium hydroxide.

[Write the equations representing the action in both cases. In what does the analogy between the decomposi-

tion of ammonium salts by bases and of carbonates by acids consist?]

2. The hydroxide or base from which the salt is derived may be insoluble or difficultly soluble in water, and not volatile.

In this case, if both the salt and the base are in solution, decomposition takes place, and the insoluble or difficultly soluble hydroxide or base is precipitated. This has already been illustrated.

3. The base from which the salt is derived may be soluble and not volatile.

In this case there is no direct evidence of change. Thus, when sodium hydroxide is added to potassium nitrate, nothing is seen except a clear solution. To determine what takes place is a difficult matter.\*

**Sulphides.**—Many sulphides are found in nature. They are made by heating metals with sulphur; by treating solutions of salts with hydrogen sulphide or soluble sulphides.

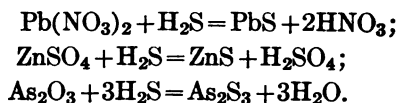
**EXAMPLES.**—Among the common natural sulphides are iron pyrites,  $\text{FeS}_2$ ; lead sulphide, or galenite,  $\text{PbS}$ ; copper

\* Here a word of warning to students. Do not forget that whenever a precipitate is formed there is something in the solution which is just as important as the precipitate. Accustom yourselves to regard every case of chemical action as a whole. The statement that a precipitate is formed when sodium hydroxide is added to a solution of an iron salt is a very imperfect description of the chemical change that takes place. Precipitates have come to be regarded in a false light, in consequence of the constant use made of them for purposes of analysis. *It must be remembered that analysis is not chemistry*, though it is essential to the study of chemistry and is an important application of the science. The art of analysis is founded upon a knowledge of the science of chemistry.

pyrites,  $\text{FeCuS}_2$ . [Examine several specimens of each, and note their general properties.]

When copper or iron is heated with sulphur the corresponding sulphides are formed. (See Experiments 10, page 13, and 114, page 288.) [For what purpose were these experiments performed?]

When hydrogen sulphide is passed through a solution containing a metal whose sulphide is insoluble, the sulphide is precipitated. This has been illustrated by passing the gas through solutions of lead nitrate, zinc sulphate, and arsenic trioxide. The reactions are:



[What differences were observed in these three cases?]

When a soluble sulphide, as ammonium sulphide or sodium sulphide, is added to a solution containing a metal whose sulphide is insoluble, the insoluble sulphide is thrown down.

#### PRECIPITATION OF SULPHIDES BY AMMONIUM SULPHIDE.

*Experiment 133.*—Add ammonium sulphide successively to dilute solutions of an iron salt, a lead salt, a copper salt. Note what takes place in each case.

**Qualitative Analysis.**—The sulphides of all the metals except those which belong to the potassium and calcium groups, and that of magnesium, are insoluble in water. Of those sulphides which are insoluble in water, some are insoluble and some are soluble in dilute hydrochloric acid. Further, of those which are insoluble in dilute hydrochloric

acid, some are soluble and some are insoluble in ammonium sulphide.

These facts furnish the basis of the method commonly employed in analyzing substances. Suppose we have a solution containing all the more common elements, and we wish to determine what is in it. Let us suppose that, on adding hydrochloric acid to it, a precipitate is formed. This precipitate is filtered off, and the filtered solution then treated with hydrogen sulphide. Those metals whose sulphides are insoluble in dilute hydrochloric acid will be precipitated. Among the elements which may be contained in this precipitate are lead, mercury, copper, tin, arsenic. The solution from which the precipitate was thrown down may still contain those metals whose sulphides are soluble in dilute hydrochloric acid. If, therefore, we filter off the precipitate and add ammonium sulphide to the filtrate, the metals whose sulphides are insoluble in neutral or alkaline solutions will be thrown down. Among these are iron, aluminium, chromium, manganese, etc. The filtrate from this precipitate may contain all those metals whose sulphides are soluble in water. By means of other reactions these can be subdivided into groups. In the ordinary method of analysis we have, therefore, several groups of elements to deal with. These are:

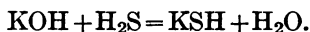
1. *The hydrochloric-acid group*, consisting of those metals whose chlorides are insoluble in water.
2. *The hydrogen-sulphide group*, consisting of those metals whose sulphides are insoluble in dilute hydrochloric acid.
3. *The ammonium-sulphide group*, consisting of those metals whose sulphides are soluble in dilute hydrochloric acid, but are precipitated by ammonium sulphide.

4. Elements whose sulphides are soluble in water.

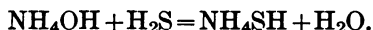
Each of these groups can be subdivided, and the subgroups again subdivided, until positive evidence of the presence of certain metals is obtained.

**Hydrosulphides** are formed when hydrogen sulphide is passed into a solution of a hydroxide until no more is taken up.

Potassium hydrosulphide is formed thus:



Ammonium hydrosulphide is formed thus:



**Nitrates.**—These salts are formed by treating metals with nitric acid; by treating oxides or hydroxides with nitric acid, and in general by treating any easily-decomposed salt as a carbonate with nitric acid.

**EXAMPLES.**—When nitric acid acts upon copper, copper nitrate is formed. [What else is formed? Give an account of the changes which take place. Write the equation representing the reaction.]

The simple neutralization of nitric acid with a base or hydroxide has been illustrated in the experiments on acids and bases (Experiment 61, page 140). [Write the equations representing the reactions which take place when nitric acid is neutralized with potassium hydroxide, with calcium oxide, with calcium hydroxide.]

All nitrates are soluble in water, and all are decomposed by heat. [Try the solubility, in water, of such nitrates as may be available.]



## NITRATES.

*Experiment 134.*—Heat about a quarter of a gram of potassium nitrate on charcoal in the blowpipe flame. The decomposition with evolution of gas is called *deflagration*. Heat some copper nitrate and powdered lead nitrate. Note the changes which take place. The compounds left behind are copper oxide and lead oxide.

**Chlorates** are made from potassium chlorate, which is made by treating a strong solution of caustic potash with chlorine. [Explain the reaction, page 127.]

Chlorates are soluble in water, and are decomposed by heat with evolution of oxygen. [When potassium chlorate is heated, what takes place in the first stage of the operation?]

*Hypochlorites* are formed by treating some of the metallic hydroxides in dilute solution with chlorine. This has been illustrated in the formation of “bleaching-powder,” which contains calcium hypochlorite. (Experiment 59, page 130. See also page 392.)

Hypochlorites are decomposed by heat.

**Sulphates.**—Some sulphates, as those of calcium and barium, are found in nature, the former being known as *gypsum*. Sulphates are made by treating metals or metallic hydroxides or oxides with sulphuric acid; by treating easily-decomposed salts, as carbonates, with sulphuric acid; and by treating a solution containing a metal whose sulphate is insoluble with sulphuric acid or a soluble sulphate.

**EXAMPLES.**—Usually, when sulphuric acid acts upon a metal, hydrogen is evolved and a salt is formed. This has been illustrated in the preparation of hydrogen by means of zinc and sulphuric acid.

## FORMATION OF IRON SULPHATE.

*Experiment 135.*—Dissolve some iron in dilute sulphuric acid. When the action is over, warm and filter the solution and allow it to crystallize. [Was hydrogen evolved during the action of the acid on the metal? What is the appearance of the salt? Does it contain water of crystallization?] Dry some of the salt, and put it aside for further use.

## FORMATION OF COPPER SULPHATE.

*Experiment 136.*—Dissolve some copper foil in concentrated sulphuric acid (see page 294). [In what respect does the action in this case differ from that in the last experiment?] When the action is over, and the mass has cooled down, pour it into three or four times its volume of hot water, when most of the black deposit will dissolve. Filter the solution, and after evaporation let the salt deposit in the form of crystals. [What is the appearance of the salt? Does it contain water of crystallization? What does the salt look like after it has been heated in a tube?] Dry some of it, and put it aside for further use. [Write the equation representing the action which takes place when copper acts upon sulphuric acid.]

The action of sulphuric acid on metallic hydroxides has been illustrated (see page 141).

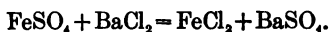
[Write the equation representing the action which takes place when the acid acts upon sodium hydroxide, potassium hydroxide, ammonium hydroxide. What is monosodium sulphate? What is neutral sodium sulphate? Is there any difference between disodium sulphate and neutral sodium sulphate?]

Most sulphates are soluble in water. The sulphates of barium, strontium, and lead are insoluble in water, and the sulphate of calcium is difficultly soluble. Therefore, when sulphuric acid is added to a solution containing either

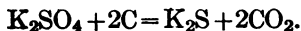
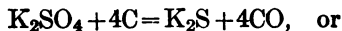
of the metals barium, strontium, or lead, a precipitate is formed.

#### FORMATION OF SULPHATES BY PRECIPITATION.

*Experiment 137.*— Make a dilute solution of barium chloride, of lead nitrate, of strontium nitrate. To a small quantity of each in a test-tube add a little sulphuric acid. In each case a white precipitate is formed. Make a somewhat concentrated solution of calcium chloride. To this add some sulphuric acid. A precipitate of calcium sulphate,  $\text{CaSO}_4$ , is formed. Add more water, and see whether this precipitate will dissolve. The formulas of the salts used in the experiments are barium chloride,  $\text{BaCl}_2$ ; lead nitrate,  $\text{Pb}(\text{NO}_3)_2$ ; strontium nitrate,  $\text{Sr}(\text{NO}_3)_2$ . The precipitates are, respectively, barium sulphate,  $\text{BaSO}_4$ , lead sulphate,  $\text{PbSO}_4$ , and strontium sulphate,  $\text{SrSO}_4$ . [Write the equations expressing the reactions.] If to the solutions of the salts any soluble sulphate is added instead of sulphuric acid, the same insoluble sulphates will be formed. The sulphates of iron, copper, sodium, and potassium are among the soluble sulphates. Make dilute solutions of small quantities of each of these, and add them separately to solutions of barium chloride, lead nitrate, and strontium nitrate. The formula of iron sulphate is  $\text{FeSO}_4$ ; of copper sulphate,  $\text{CuSO}_4$ ; of sodium sulphate,  $\text{Na}_2\text{SO}_4$ ; and of potassium sulphate,  $\text{K}_2\text{SO}_4$ . Write the equations representing the reactions which take place in the above experiments. It need hardly be explained that the action consists in an exchange of places on the part of the metals. Thus, when the soluble salt, iron sulphate,  $\text{FeSO}_4$ , is brought together with the soluble salt, barium chloride,  $\text{BaCl}_2$ , the insoluble salt, barium sulphate,  $\text{BaSO}_4$ , and the soluble salt, iron chloride,  $\text{FeCl}_2$ , are formed:



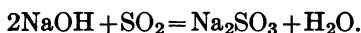
When heated with charcoal in the reducing flame of the blowpipe, sulphates are reduced to sulphides:



## REDUCTION OF A SULPHATE TO A SULPHIDE.

*Experiment 138.*—Mix and moisten a little sodium sulphate and finely-powdered charcoal. Heat the mixture on charcoal in the reducing flame of a blowpipe. After cooling, scrape off the salt from the charcoal, dissolve it in a few cubic centimetres of water, and filter through a small filter. If the change to the sulphide has taken place, sodium sulphide,  $\text{Na}_2\text{S}$ , is in solution. Add several drops of a solution of a copper salt to some of the solution of the sulphide and heat to boiling, when a black precipitate of copper sulphide will be formed. Also try the action of a drop of the solution of sulphide on a bright silver coin.

**Sulphites** are made from sodium or potassium sulphite, which are made by treating sodium or potassium hydroxide in solution with sulphur dioxide:



All sulphites are decomposed by the common acids, sulphur dioxide being given off:



**Carbonates.**—Many carbonates are found in nature, some of them in great abundance, and widely distributed. The principal one is calcium carbonate. They are made by passing carbon dioxide into solutions of hydroxides, and by adding soluble carbonates to solutions of salts containing metals whose carbonates are insoluble.

**EXAMPLES.**—The formation of potassium carbonate by the treatment of potassium hydroxide with carbon dioxide has already been illustrated. (See Experiment 93, page 234.)

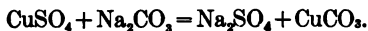
[Write the equation representing the action. Is the salt formed in this case soluble or insoluble in water?]

The formation of calcium carbonate by passing carbon dioxide into a solution of calcium hydroxide (lime-water) has been illustrated under Carbon Dioxide.

[Describe the experiment. Write the equation representing the action in this case. Is calcium carbonate soluble or insoluble in water? In hydrochloric acid, in sulphuric acid, in nitric acid? What action takes place when it is treated with each of these acids?]

#### FORMATION OF CARBONATES BY PRECIPITATION.

*Experiment 139.*—The formation of carbonates by the addition of soluble carbonates to solutions of salts of metals whose carbonates are insoluble is illustrated by the following experiments: Make dilute solutions of copper sulphate, iron sulphate, lead nitrate, silver nitrate, calcium chloride, barium chloride. Add to each a little of a solution of a soluble carbonate, as sodium carbonate, potassium carbonate, ammonium carbonate. Note the result in each case. Filter off all the precipitates, wash them thoroughly by means of a fine stream of water from a wash-bottle (see Appendix I) and determine whether they are carbonates. This may be done by treating them with dilute acids, which decompose them, causing an evolution of carbon dioxide, which can be detected by passing a little of it into lime-water. Write all the equations representing the reactions that take place in the above experiments. Here again, as in the experiments with the sulphates, the metals exchange places:



[Is copper bivalent or univalent if the formula of copper sulphate is  $\text{CuSO}_4$ ?]

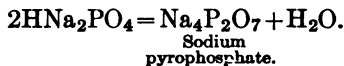
All carbonates except those of the members of the potassium family are insoluble, and are decomposed by heat into carbon dioxide and the oxide of the metal. The decom-

position of calcium carbonate into lime and carbon dioxide is the best-known illustration of this fact:

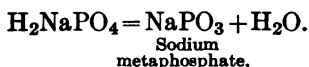


**Phosphates.**—Calcium phosphate is very abundant in nature, and a few other phosphates are also found. The methods of making phosphates are in principle the same as those used in making sulphates.

The phosphates of all the metals except the members of the potassium family are insoluble in water. The normal phosphates [What is a normal phosphate? (see page 311)], as a rule, are not changed by heat. Those phosphates in which two thirds of the hydrogen is replaced by metal—as, for example, disodium phosphate,  $\text{HNa}_2\text{PO}_4$ —lose water when heated, and yield pyrophosphates:



Those phosphates in which only one third of the hydrogen is replaced by metal—as, for example, monosodium phosphate,  $\text{H}_2\text{NaPO}_4$ —lose water when heated, and yield metaphosphates:



Neither the pyrophosphates nor the metaphosphates are changed by heat.

**Silicates.**—The extensive occurrence of silicates in nature has been spoken of. Those which are most abundant are

the *feldspars* and their decomposition-products. The principal feldspar is a complex silicate of aluminium and potassium, of the formula  $\text{KAlSi}_3\text{O}_8$ , derived from the polysilicic acid  $\text{H}_4\text{Si}_3\text{O}_8$  [What is a polysilicic acid? (see page 321)]:

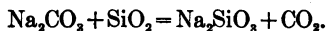


Silicates can be made by heating together at a high temperature silicon dioxide, in the form of fine sand, and bases.

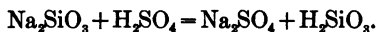
Some silicates are decomposed by the ordinary acids, such as sulphuric and nitric acids, the silicic acid separating as a difficultly soluble substance, which loses water and becomes insoluble.

#### SILICIC ACID.

*Experiment 140.*—Heat a mixture of potassium and sodium carbonates in a platinum crucible in the flame of the blast-lamp \* until the mass is thoroughly melted. Add fine sand slowly to the fused mass. When it has cooled down, boil the dish and its contents in water. Filter to remove the excess of sand. A mixture of potassium and sodium silicates passes into solution:



*Experiment 141.*—Treat a little of the solution containing sodium and potassium silicates, prepared in the last experiment, with a little sulphuric or hydrochloric acid. A gelatinous substance will be precipitated. This is silicic acid. Some of the acid remains in solution:

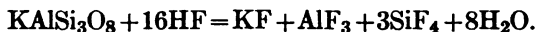


By evaporating the solution to dryness and heating for a time on the water-bath all the silicic acid is converted into silicon dioxide, which is entirely insoluble.

\* This is a large blowpipe worked by a foot-bellows.

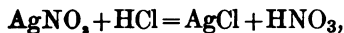
Many silicates that are not acted upon by strong acids are decomposed when fused with sodium or potassium carbonate.

Silicates which are not decomposed in either of the ways mentioned yield to hydrofluoric acid. The action consists in the formation of the gas, silicon tetrafluoride,  $\text{SiF}_4$ , and the fluorides of the metals present. Thus, the reaction in the case of feldspar takes place according to the equation



The silicon fluoride is given off and the fluorides of the metals are soluble in water. Hence hydrofluoric acid *dissolves* the silicate. [Is this use of the word *dissolves* strictly correct?]

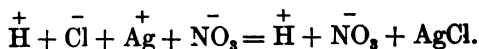
**Reactions in Solution are Reactions of Ions.**—While in the account given in this chapter of the methods of making the compounds of the metals, the equations used have represented the compounds as acting upon one another, it is clear from what has already been said (see page 143) in regard to reactions that take place in solution, in water at all events, that we can go a step farther in expressing what takes place in these reactions. The reactions are believed to take place between the ions that are formed when the substances pass into solution. Thus, when hydrochloric acid dissolved in water acts upon silver nitrate dissolved in water the equation



while telling the truth, does not tell the whole truth as the matter is now understood. For in the solution of hydrochloric acid the ions H and Cl are present; and, in the solu-



tion of silver nitrate, the ions  $\text{Ag}^+$  and  $\text{NO}_3^-$ . Consequently, reaction must take place between these. It is expressed thus:



The substance represented by the formula  $\text{AgCl}$ , silver chloride, is insoluble in water, and is therefore removed from the field of action, while the ions  $\text{H}$  and  $\text{NO}_3$  remain, forming what is usually called a solution of nitric acid.

Bearing in mind the fact that acids, in general, dissociate in solution into hydrogen ions and into other ions the composition of which depends upon the composition of the acid; that bases dissociate into hydroxyl ions and, generally, metallic ions; and that salts dissociate into metallic ions and the ions which in acids are in combination with hydrogen, there is no difficulty in translating an ordinary chemical equation into an ionic equation.

## CHAPTER XX.

### THE POTASSIUM GROUP: LITHIUM, SODIUM, POTASSIUM, CÆSIUM, RUBIDIUM (AMMONIUM).

**General.**—The most widely-distributed and hence best-known members of this group are sodium and potassium. The hypothetical metal ammonium is included in the group because the salts formed by ammonia, in which this hypothetical metal is regarded as present, resemble the salts of potassium and sodium. The members of the group are generally called the *metals of the alkalis*, as the two best-known members are obtained from the alkalis, caustic potash and caustic soda, or potassium and sodium hydroxides.

**Potassium, K (At. Wt. 39).**—This element is a constituent of many minerals, particularly of feldspar, which, as already explained (page 353), is a complex silicate of aluminium and potassium. It is found also in combination with chlorine as sylvite; and with chlorine and magnesium as carnallite, particularly in the great Stassfurt deposits; with sulphuric acid and aluminium, as alum; with nitric acid, as saltpetre or potassium nitrate; and in other forms. The natural decomposition of minerals containing potassium gives rise to the presence of this metal, in various forms of combination, everywhere in the soil. It is taken up by plants; and when vegetable material is burned the potassium remains behind, chiefly as potassium carbonate. When

wood-ash is treated with water the potassium carbonate is dissolved, and it is obtained in an impure state by evaporating the solution. The substance thus obtained is called *potash*. In the juice of the grape there is contained a salt of potassium, mono-potassium tartrate, or "cream of tartar," which is deposited in large quantity from wine. This is commonly called "crude tartar."

## POTASSIUM.

*Experiment 142.*—If convenient treat two or three litres of wood-ashes with water. Filter off the solution and examine it by means of red litmus-paper. The color of the paper is changed to blue. Plainly the solution is alkaline. Examine some potassium carbonate. [Does its solution act in the same way?] Evaporate the solution to dryness. Collect the dry residue and treat it with dilute hydrochloric acid. [Is a gas given off? Is it carbon dioxide?]

**Preparation.**—The metal was first prepared by Sir Humphry Davy, in the year 1807, by the action of a powerful electric current on potassium hydroxide. It is now manufactured by the action of an electric current on potassium hydroxide, cyanide, or chloride.

**Properties.**—It is a light substance, that floats on water. [Have you had evidence of this?] Its freshly-cut surface has a bright metallic lustre, almost white; it acts upon water with energy, causing the evolution of hydrogen, which burns, and the formation of potassium hydroxide. This reaction has already been treated of in connection with hydrogen. [Turn back to the experiment (Experiment 27, page 45) and perform it again. It will now appear much

clearer.] In consequence of its action on water, potassium cannot be kept in the air. It is kept under some oil upon which it does not act, as, for example, petroleum.

**Compounds of Potassium.**—The chief compounds of potassium met with are the *iodide*, KI, which is extensively used in medicine and in photography; the *hydroxide*, or caustic potash, KOH, which finds extensive use in laboratories; the *nitrate*, or saltpetre,  $\text{KNO}_3$ , used in the manufacture of gunpowder; the *chlorate*,  $\text{KClO}_3$ , used in the preparation of oxygen and in medicine; the *cyanide*, KCN; and the *carbonate*,  $\text{K}_2\text{CO}_3$ .

The methods used in preparing some of these compounds are interesting, as illustrating the applications of the principles of chemistry.

**Potassium Iodide**, KI, is made by treating caustic potash with iodine until the solution begins to show a permanent yellow color, which is an indication that no more iodine will be taken up. The action is the same in character as that which takes place when chlorine acts upon warm concentrated caustic potash. Both the iodide and iodate are formed:



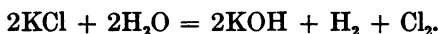
By evaporating off the water and heating the residue, the iodate is decomposed, giving the iodide and oxygen.

#### POTASSIUM IODIDE.

*Experiment 143.*—Examine a bottle of crystallized potassium iodide. Taste a little. Dissolve some in water. Add some

iodine to this solution. [Does the iodine dissolve?] Heat a little. [Does it contain water of crystallization?] Treat a crystal or two with a few drops of concentrated sulphuric acid. [What takes place? To what is the appearance of violet vapors due? (See Experiment 109, page 276).]

**Potassium Hydroxide, KOH.**—This well-known substance, commonly called caustic potash, is prepared by the action of an electric current on a concentrated solution of potassium chloride:

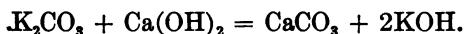


It can also be made by treating potassium carbonate with calcium hydroxide in a silver or iron vessel.

#### POTASSIUM HYDROXIDE.

*Experiment 144.*—Dissolve 50 grams potassium carbonate in 500 to 600 cc. water. Heat to boiling in an iron or silver vessel, and gradually add the slaked lime obtained from 25 to 30 grams of good quick-lime. During the operation the mass should be stirred with an iron spatula. After the solution is cool, draw it off by means of a siphon into a bottle. This may be used in experiments in which caustic potash is required. It must be protected from the air or it will be converted into carbonate.

The reaction is based upon the fact that calcium carbonate is insoluble, and that potassium carbonate and calcium hydroxide are soluble:



The chief application of potassium hydroxide outside of the laboratory is for making soft-soap. For this purpose fats are boiled with a solution of potassium hydroxide or carbonate.

The hydroxide is a white brittle substance. In contact with the air it deliquesces [What does this mean? (see page 57)] and absorbs carbon dioxide. It is a very strong base. [Explain the action that takes place when potassium hydroxide acts upon ammonium chloride,  $\text{NH}_4\text{Cl}$ ; copper sulphate,  $\text{CuSO}_4$ ; and magnesium nitrate,  $\text{Mg}(\text{NO}_3)_2$ .]

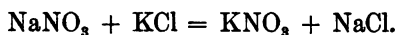
**Stassfurt Potash Industry.**—Practically all potassium hydroxide is now made from Stassfurt carnallite electrolytically. Indeed, most of the potassium salts are made from these deposits. The average yearly production of crude Stassfurt salts is shown in the following table:

Carnallite, $\text{MgCl}_2\cdot\text{K}$ .....	1,816,733 tons.
Kainite, $\text{MgSO}_4\cdot\text{KCl}$ and Schönite, $\text{K}_2\text{Mg}(\text{SO}_4)_2$ .....	1,450,020 “
Sylvite, $\text{KCl}$ .....	191,448 “
Kieserite, $\text{MgSO}_4$ .....	1,763 “

Nearly all the carnallite and kieserite are used for technical purposes.

**Potassium Nitrate,  $\text{KNO}_3$ .**—This salt is commonly called *saltpetre*. Its occurrence in nature has already been referred to under Nitric Acid, page 178. When refuse animal matter is left to undergo decomposition in the presence of bases, nitrates are always the end-products. Advantage was formerly taken of this fact for the purpose of preparing saltpetre artificially, the process being carried on on the large scale in the “saltpetre plantations.” In these, refuse animal matter is mixed with earthy material, wood-ashes, etc., and piled up. These piles are moistened with

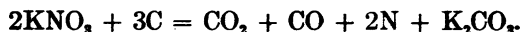
the liquid products from stables. After the action has continued for two or three years the outer crust is taken off and extracted with water. The solution thus obtained contains besides potassium nitrate, calcium and magnesium nitrates. It is treated with a water-extract of wood-ashes or with potassium carbonate, by which the calcium and the magnesium are precipitated as carbonates. This process is now of very little importance. Most of the saltpetre which is in the market is made from Chili saltpetre (see page 369,) or sodium nitrate, by treating it with potassium chloride:



Potassium nitrate crystallizes in long, rhombic prisms of salty taste.

**Uses of Potassium Nitrate.**—Potassium nitrate is used as an oxidizing agent in the laboratory, and in the manufacture of fireworks. Its chief use, however, is in the manufacture of gunpowder.

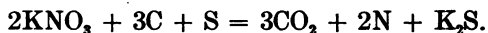
**Gunpowder.**—The value of gunpowder is due to the fact that it *explodes* readily, the explosion being a chemical change accompanied by a sudden evolution of gases. Gunpowder is made of a mixture of saltpetre, charcoal, and sulphur. When heated, the saltpetre gives off oxygen and nitrogen; the oxygen combines with the charcoal, forming carbon dioxide and carbon monoxide, and the sulphur combines with the potassium, forming potassium sulphide. When a mixture of saltpetre and charcoal is burned, the reaction that takes place is this:



#### BURNING OF A MIXTURE OF POTASSIUM NITRATE AND CHARCOAL.

*Experiment 145.*—Mix 15 grams finely-powdered potassium nitrate and 2.5 grams powdered charcoal. Set fire to the mass in an iron vessel.

By adding the necessary quantity of sulphur the carbon dioxide, which would otherwise remain in combination with the potassium as potassium carbonate, is given off and potassium sulphide is formed:



For this reaction the constituents should be mixed in the proportions:

Saltpetre .....	74.82
Charcoal .....	13.33
Sulphur .....	11.85
	100.00

[PROBLEM.—What would be the volume, at 0° and under 76° mm. pressure, of the gases evolved from 5 grams of gunpowder containing the constituents in exactly the proportions given above?]

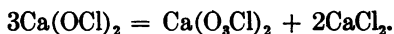
This is approximately the composition of all powder. When gunpowder explodes, the gases formed occupy about 280 times the volume occupied by the powder itself.

The use of gunpowder is decreasing rapidly. For guns and cannon it is practically entirely replaced by *smokeless powder* (which see), and for mining and blasting by gun-cotton, dynamite, and similar explosives.

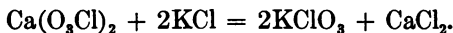
**Potassium Chlorate,  $\text{KClO}_3$ .**—The reactions by which



potassium chlorate is formed when chlorine acts upon a solution of potassium hydroxide have been discussed (see pp. 126, 127). In the manufacture of the chlorate it is found advantageous first to make calcium chlorate, and then to treat this with potassium chloride, when, at the proper concentration, potassium chlorate crystallizes. The process in brief consists in passing chlorine into a solution of calcium hydroxide in which an excess of hydroxide is held in suspension. The first action leads to the formation of calcium hypochlorite. When the solution of this salt is boiled, it is decomposed yielding the chlorate and chloride:



On now treating the solution with potassium chloride the following reaction takes place:



**Properties.**—Potassium chlorate gives up oxygen very easily and is hence a good oxidizing agent. It dissolves in water at the ordinary temperatures to the extent of 6 parts in 100 of water.

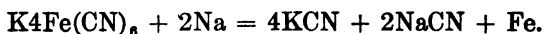
**Uses.**—The chief uses of potassium chlorate are in the preparation of oxygen, and in the manufacture of matches and fireworks. The tips of Swedish safety-matches are made of potassium chlorate and antimony sulphide. The surface upon which they are rubbed to ignite them contains red phosphorus. The chlorate is extensively used in medicine, particularly as a gargle for sore throat.

**Potassium Cyanide, KCN.**—This salt is made by heating potassium ferrocyanide or yellow prussiate of potash,  $K_4Fe(CN)_6$ , with potassium and extracting the mass with water. It is a violent poison. Much of the potassium cyanide found in the market is made by heating potassium ferrocyanide with sodium and therefore contains a large percentage of sodium cyanide.

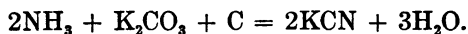
The reaction when potassium is used is this:



When sodium is used it is this:



Potassium cyanide is made technically by conducting ammonia over a mixture of potassium carbonate and carbon at high temperature:



It is used in great quantities in the cyanide process for the extraction of gold from its ores (see Gold), in gold, silver and nickel plating, and in photography as a solvent for silver salts.

**Potassium Sulphate,  $K_2SO_4$ .**—This salt occurs in combination with others in nature, particularly in the mineral *kainite*, which has the composition  $K_2SO_4.MgSO_4.MgCl_2 + 6H_2O$ . The principal source of this compound is Stassfurt, Germany. Potassium sulphate is used in medicine, and in the preparation of ordinary alum and of potassium carbonate.

Potassium sulphate is made technically at Stassfurt, chiefly for use as fertilizer, by adding to a solution of schönite or leonite potassium chloride:  $K_2Mg(SO_4)_2 + 2KCl = MgCl_2 + 2K_2SO_4$ . As magnesium chloride is much more soluble than potassium sulphate the latter crystallizes out. It is also made similarly from kainite,  $MgSO_4 \cdot KCl + 3H_2O$ , by adding potassium chloride.

**Sodium, Na** (At. Wt. 23).—Sodium occurs very widely distributed and in large quantities, principally as sodium chloride. It is found in a number of silicates, and is a constituent of plants, especially of those which grow in the neighborhood of the seashore and in the sea. Just as the ashes of inland plants are rich in potassium carbonate, so the ashes of sea-plants and those which grow near the sea are rich in sodium carbonate. It is found everywhere in the soil, but generally in small quantity, its presence being due to the decomposition of minerals containing it, such as soda feldspar, or albite. It occurs also as sodium nitrate, and in large quantity in Greenland as *cryolite*,  $Na_3AlF_6$ , or  $AlF_3 \cdot 3NaF$ .

**Preparation.**—Sodium is generally prepared by the electrolysis of fused sodium hydroxide, the sodium going to the cathode and the hydroxyl to the anode where it decomposes into water and hydrogen. The water thus set free attacks the sodium, regenerating hydroxide so that the practical yield is only about 40 per cent of the theoretical.

**Properties.**—Its properties are similar to those of potassium. It is light, floating on water (see page 44); it has a bright metallic lustre, and is soft. It decomposes water, but not as actively as potassium.

[Describe what takes place when potassium acts upon water and when sodium acts upon water. How is the difference accounted for?]

**Applications.**—It is used in obtaining gold from its ores, as sodium cyanide (which see) and as sodium amalgam, further for making sodium peroxide, and for technical organic synthesis. It is used in the laboratory for the purpose of isolating some elements whose oxides cannot easily be reduced, as, for example, aluminium, magnesium, and silicon, which are prepared by treating their chlorides with sodium. Silicon, however, is more readily prepared by treating potassium fluosilicate,  $K_2SiF_6$ , with sodium. The element is also used in combination with mercury as sodium amalgam, a substance which affords a ready means of making nascent hydrogen. It also finds constant application in the laboratory for a variety of purposes.

**Compounds of Sodium.**—The chief compounds of sodium are the *chloride*,  $NaCl$ ; the *hydroxide*, or caustic soda,  $NaOH$ ; the *peroxide*,  $Na_2O$ ; the *nitrate*, or Chili saltpetre,  $NaNO_3$ ; the *sulphate*,  $Na_2SO_4$ ; the *thiosulphate*,  $Na_2S_2O_3$ ; the *carbonate*,  $Na_2CO_3$ ; the *cyanide*,  $NaCN$ ; the *borate*, or borax,  $Na_2B_4O_7$ ; the *phosphate*,  $HNa_2PO_4$ ; and the *silicate*,  $Na_2SiO_3$ .

**Sodium Chloride,  $NaCl$ .**—This is the substance which is known as *salt*, or *common salt*. It occurs very widely dis-

tributed, and, as it is easily soluble, much of the water that enters into the ocean contains some of it in solution. Sea-water contains from  $2\frac{1}{2}$  to 3 per cent. The most important deposits are those at Wieliczka in Galicia, at Stassfurt and Reichenhall in Germany, and at Cheshire in England. Besides these there are, however, many other deposits in the United States, in Africa, and in Asia. In the United States it is mined in New York near Syracuse, in Michigan, near Saginaw Bay and Manistee. Brine is evaporated near Salina, Kansas, and there are deposits in the valley of the Ohio River, near Pomeroy and Wheeling. In some places the salt is taken out of the mines in solid form; in others, water is allowed to flow into the mines, and to remain for some time in contact with the salt. The solution thus formed is drawn or pumped out of the mine, and evaporated by appropriate methods. In hot countries salt is obtained by the evaporation of sea-water, the heat of the sun being utilized for the purpose. Large shallow cavities are made in the earth, and into these the water flows at high tide, or it is pumped up into them.

**Properties.**—Sodium chloride crystallizes in colorless and transparent cubes. Sometimes that which occurs in nature is colored blue. In hot water it is but little more soluble than in cold water. In crystallizing, the crystals enclose water, not as water of crystallization, and this is given off when the crystals are heated, the action being accompanied by a crackling sound. This phenomenon is known as *decrepitation*. Pure sodium chloride is not deliquescent. Most salt contains a little magnesium chloride which is deliquescent. Hence the annoying peculiarity of table salt

U. S. N.

at the seashore or in moist weather. Salt can be obtained that does not show this peculiarity.

**Uses.**—Salt is used as the starting-point in the preparation of all sodium compounds and of chlorine and hydrochloric acid. Salt is necessary to the life of man and many other animals.

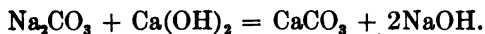
[How are chlorine and hydrochloric acid obtained from it? What takes place when a solution of silver nitrate is added to a solution of common salt? What substances besides silver nitrate act in the same way?]

The great salt-producing countries in the order of production are the United States, Great Britain, Russia, Germany, France, and India. The production, in tons, of these countries for 1904 was:

United States.	Gt. Britain.	Russia (1902.)
3,084,000.	2,118,000.	2,036,000.
Germany.	France.	India.
1,875,000.	1,292,000,	1,237,000.

The total production for 1904 was 14,728,000 tons. Michigan and New York each produces over a third of the total production of the United States.

**Sodium Hydroxide, NaOH.**—This compound resembles potassium hydroxide in most respects. Being cheaper it is used more extensively. It is prepared in the same way, by treating sodium carbonate in solution with calcium hydroxide, when insoluble calcium carbonate and soluble sodium hydroxide are formed:



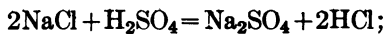
It is now prepared chiefly by the electrolysis of sodium chloride, either by the use of a mercury cathode (see Chlorine), when the hydroxide is obtained in solution, or by the Acker process in use at Niagara Falls. In this interesting and successful process the temperature is above  $400^\circ$  and the cathode is molten lead. The sodium dissolves in the molten lead which flows off as the solution becomes concentrated, fresh lead flowing in to replace it. By directing a jet of steam on the sodium-lead alloy the reaction,  $2\text{Na} + 2\text{H}_2\text{O} = 2\text{NaOH} + \text{H}_2$ , occurs, forming pure *molten* sodium hydroxide which is run into moulds while the lead flows again to form the cathode. The chlorine is obtained at the anode in this process as well as in the others. *Chemically pure sodium hydroxide* is generally made by the action of sodium on pure water. Sodium hydroxide is commonly called *caustic soda*. It is extensively used for the purpose of making soap from fats.

**Sodium Peroxide,  $\text{Na}_2\text{O}_2$ .**—This substance has recently come into the market as a bleaching material. It is made by passing purified air over fused metallic sodium heated to  $300^\circ$ . It dissolves in dilute acids *in the cold* and gives a strong solution of hydrogen peroxide. A fused form of sodium peroxide prepared by a patented process is known as "oxone" (see page 28). This gives off oxygen when treated with water.

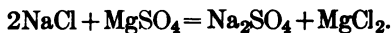
**Sodium Nitrate,  $\text{NaNO}_3$ .**—This compound occurs in large quantity in southern Peru, on the border of Chili, and is known as Chili saltpetre. The natural salt contains, be-

sides the nitrate, sodium chloride, sulphate, and iodide. Sodium nitrate is very similar to potassium nitrate, but it cannot be used in place of the more expensive potassium salt in the manufacture of the finer grades of gunpowder, as it becomes moist in the air and does not decompose quickly enough. It is used extensively in the manufacture of nitric acid, and also for the purpose of preparing ordinary saltpetre. The iodine contained in it is extracted on the large scale, and this forms an important source of iodine. The chief use of sodium nitrate is as a fertilizer.

**Sodium Sulphate,  $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ .**—The common name of this substance is Glauber's salt. It is made on the large scale by the action of sulphuric acid on sodium chloride:



and by the action of magnesium sulphate on sodium chloride:



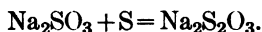
The salt crystallizes in large colorless monoclinic prisms, containing 10 molecules of water of crystallization,  $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ . It loses water when left in contact with the air. [Is it efflorescent or deliquescent?]

It is extensively used in the manufacture of glass.

**Sodium Thiosulphate,  $\text{Na}_2\text{S}_2\text{O}_3 + 5\text{H}_2\text{O}$ .**—This is the salt commonly called *hyposulphite of soda*. It is made on the large scale by treating caustic soda with sulphur, and conducting sulphur dioxide into the solution. It is also made



by adding sulphur to a boiling solution of sodium sulphite:

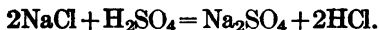


Its chief use is in photography, in which art it is generally called "hypo." Its use will be explained under Photography (which see).

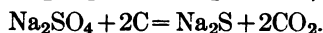
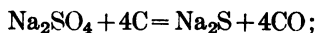
**Sodium Carbonate,**  $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$ .—This salt, commonly called *soda*, is one of the most important of manufactured chemical substances. The mere mention of the fact that it is essential to the manufacture of glass and soap will serve to give some conception of its importance. It is found in the ashes of sea-plants, just as potassium carbonate is found in the ashes of those plants which grow on the land. We are, however, not dependent on sea-plants for our supply, as two methods have been devised for preparing sodium carbonate from sodium chloride with which nature provides us in such abundance. As these methods are interesting applications of chemical principles, it will be well to consider them briefly.

**The Le Blanc Process.**—The problem to be solved is to convert sodium chloride,  $\text{NaCl}$ , into sodium carbonate,  $\text{Na}_2\text{CO}_3$ . The process devised by Le Blanc for the French government during the Revolution, when the supply had been cut off, involves four reactions that take place in three stages:

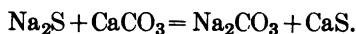
1st. The sodium chloride is converted into sodium sulphate by treating it with sulphuric acid:



2d. The sodium sulphate thus obtained is heated with charcoal, which reduces it to sodium sulphide,  $\text{Na}_2\text{S}$ :



3d. The sodium sulphide is heated with calcium carbonate, when sodium carbonate and calcium sulphide are formed:



Calcium sulphide is insoluble in water containing lime, so that by treating the resulting mass with water the sodium carbonate is separated from the sulphide.

In practice the sodium sulphate is mixed with coal and calcium carbonate, and the mixture heated. The coal reduces the sulphate to the sulphide, which acts upon the calcium carbonate, forming sodium carbonate and calcium sulphide. The product of the action is known as *crude soda* or *black ash*. In order to purify this product, it is broken into pieces, and treated with water. Soda comes into the market as *calcined purified soda*, which contains no water of crystallization, and as *crystallized soda*, which has the composition  $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$ .

This process is now only in use in England.

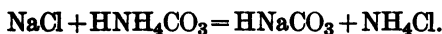
As, in the manufacture of soda by the Le Blanc process, the sulphur remains in combination as calcium sulphide, a process, known as the Chance process, has been devised for its recovery. This consists in passing carbon dioxide into the waste, thus liberating hydrogen sulphide; pass-

ing this into another portion of the waste, thus converting the calcium sulphide into the hydrosulphide; and then treating this with carbon dioxide, when a gas rich in hydrogen sulphide is given off:



By regulating the supply of air the gas is burned either to sulphur dioxide which is conducted into the sulphuric acid chambers (see page 310) or to sulphur.

**The Solvay or Ammonium Process.**—Another and cheaper process is the so-called *ammonia-soda process*, or the *Solvay process*. This depends upon the fact that monosodium carbonate,  $\text{HNaCO}_3$ , is comparatively difficultly soluble in water. If, therefore, monoammonium carbonate, or acid ammonium carbonate,  $\text{HNH}_4\text{CO}_3$ , is added to a solution of common salt, acid sodium carbonate,  $\text{HNaCO}_3$ , is precipitated, and ammonium chloride remains behind in the solution:



When the acid carbonate is heated, it gives off carbon dioxide, and is converted into the normal salt thus:



The carbon dioxide given off is passed into ammonia and thus again obtained in the form of acid ammonium carbonate:



The ammonium chloride obtained in the first reaction is treated with lime or magnesia,  $MgO$ , and the ammonia set free. This ammonia is again used in the preparation of acid ammonium carbonate.

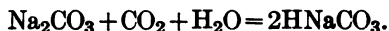
The greater part of the soda supply of the world is now furnished by the Solvay process.

#### PREPARATION OF SODIUM CARBONATE BY THE SOLVAY PROCESS.

*Experiment 146.*—Make a saturated solution of common salt in ordinary ammonia-water (about 50 cc.). Pass carbon dioxide into this solution until no more is absorbed, the delivery-tube being as in Exp. 58. Filter off the precipitate, and dry it by spreading it upon layers of filter-paper. Heat some of the salt when dry, and determine whether the gas given off is carbon dioxide or not. When gas is no longer given off by heat, let the tube cool and examine the residue. [Is it a carbonate?]

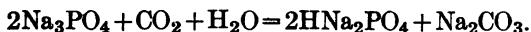
**Properties.**—Sodium carbonate crystallizes in large monoclinic prisms with 10 molecules of water of crystallization. The crystals are efflorescent.

**Monosodium Carbonate, Primary Sodium Carbonate,  $NaHCO_3$ .**—This salt is commonly called "*bicarbonate of soda*." It is easily prepared by passing carbon dioxide over the ordinary carbonate dissolved in its water of crystallization:



When heated it gives off carbon dioxide and water, and is converted into the normal salt. It is used in medicine, and extensively in the preparation of soda-water and other effervescent drinks and in baking-powders.

**Disodium Phosphate,  $\text{HNa}_2\text{PO}_4 + 12\text{H}_2\text{O}$ .**—This is the common form of sodium phosphate. It is formed when phosphoric acid is treated with sodium carbonate until the solution begins to show an alkaline reaction with red litmus. It is a remarkable fact that, although phosphoric acid is tribasic, and with most metals forms salts that are derived from the acid by replacement of all the three hydrogen atoms, as  $\text{Ag}_3\text{PO}_4$ ,  $\text{Ca}_3(\text{PO}_4)_2$ , etc., with sodium its most stable salt is the one in which sodium is substituted for two hydrogen atoms. A salt of the formula  $\text{Na}_3\text{PO}_4$  can be made, but it has an alkaline reaction, and absorbs carbon dioxide from the air, being converted into sodium carbonate and disodium phosphate:



**Sodium Borate,  $\text{Na}_2\text{B}_4\text{O}_7 + 10\text{H}_2\text{O}$ .**—This salt has been referred to under Boric Acid. It is commonly called *borax*. It is found in nature in several lakes in Asia, and in this country in Clear Lake, Nevada, and in California. It is manufactured by neutralizing the boric acid found in Tuscany.

When heated, borax puffs up, and at red heat melts, forming a transparent colorless liquid. This is anhydrous borax,  $\text{Na}_2\text{B}_4\text{O}_7$ . Molten borax has the power to dissolve metallic oxides, and forms colored glasses with some of them. It is used in blowpipe work (see Boric Acid). As it dissolves metallic oxides, it is used in the process of soldering, as it is necessary to have bright, untarnished metallic surfaces in order that the solder shall adhere firmly.

**Production of Borates.**—The salts of boric acid and their occurrence is shown in the following table of the world's production for 1902:

United States, Calcium borate..	18,148 tons.
Bolivia,                   "       "	14,437 "
Peru,                   "       "	4,156 "
Italy, Boric acid .....	2,763 "
Germany Boracite (Magnesium borate) .....	196 "
	<hr/> 39,700 "

In 1906 the United States alone produced 58,173 tons calcium borate. All the crude material is worked up into borax or boric acid in refineries.

Borax is chiefly used instead of soap as a cleansing agent. It is also extensively used in the manufacture of porcelain and in glass-painting. It is an antiseptic, preventing the decomposition of some organic substances.

**Sodium Cyanide** is made on the large scale by the action of ammonia on metallic sodium and carbon. It is used for the same purposes as potassium cyanide.

**Ammonium Salts.**—The method of formation of the so-called ammonium salts has been described (see Ammonia). These salts resemble the salts of potassium and sodium in many respects, and they are hence described in this connection. The chief ones are the sulphate,  $(\text{NH}_4)_2\text{SO}_4$ ; the chloride,  $\text{NH}_4\text{Cl}$ ; the carbonate,  $(\text{NH}_4)_2\text{CO}_3$ ; the sulphide,  $(\text{NH}_4)_2\text{S}$ ; the hydrosulphide,  $(\text{NH}_4)\text{HS}$ ; and sodium-ammonium phosphate,  $\text{NaNH}_4\text{PO}_4 + 4\text{H}_2\text{O}$ .

**Ammonium Sulphate**,  $(\text{NH}_4)_2\text{SO}_4$ , is technically the most important of ammonium salts. It is the substance from which other ammonium compounds are generally made, and as a fertilizer it is used in rapidly increasing quantities. It is made chiefly from the ammonia of coking ovens, and by distilling sea-weed with steam. The yearly production is over 500,000 tons.

**Ammonium Chloride**,  $\text{NH}_4\text{Cl}$ .—This salt is often called *sal ammoniac*. At present its principal source is the gas-works. The ammonia-water of the works is neutralized with hydrochloric acid, and the salt obtained by evaporation. It has a sharp, salty taste, and is easily soluble in water. When heated it is converted into vapor without melting, and with very slight decomposition; and when the vapor comes in contact with a cold surface, it condenses in the form of crystals. This process of vaporizing and condensing a solid is called *sublimation*.

#### SUBLIMATION OF AMMONIUM CHLORIDE.

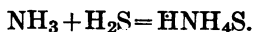
*Experiment 147*.—On a piece of platinum foil or porcelain heat a little ammonium chloride. It will pass off and form a dense white cloud. This is the same cloud that is formed by bringing together gaseous ammonia and hydrochloric acid. All ammonium salts are either volatile or decompose when heated.

[What takes place when ammonium chloride is treated with caustic soda? with lime? with sulphuric acid?]

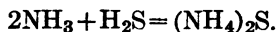
**Ammonium Sulphide**,  $(\text{NH}_4)_2\text{S}$ .—This substance is extensively used in chemical analysis for the purpose of precipitating those sulphides which are soluble in dilute hydrochloric acid. As will be remembered, in analyzing a mix-

ture of substances the first thing usually done is to add hydrochloric acid to the solution. This precipitates silver, lead, and, under certain conditions, mercury. This precipitate having been filtered off, hydrogen sulphide is passed through the filtrate, when those metals whose sulphides are insoluble in dilute hydrochloric acid are thrown down. The precipitate is filtered off and ammonium sulphide added to the filtrate, when the metals whose sulphides are soluble in dilute hydrochloric acid are thrown down. Among these are iron, cobalt, nickel, manganese, etc. Any other soluble sulphide might be used, but the advantage of ammonium sulphide is that it is volatile, and, hence, by evaporating the solution and heating, it can be got rid of so that it will not be in the way in subsequent chemical operations.

Ammonium sulphide is made by passing hydrogen sulphide into an aqueous solution of ammonia. If the gas is passed in until the solution is saturated, the product is the hydrosulphide  $\text{HNH}_4\text{S}$ :



If only half this quantity of the gas is passed in, the product is the sulphide:

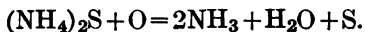


The simplest way to make the sulphide is to divide a quantity of a solution of ammonia into two equal parts. Saturate one half, thus forming the hydrosulphide, and add the other half, when this reaction takes place:





The product is a colorless liquid of a disagreeable odor. It soon changes color, becoming yellow, and after a time a yellow deposit is formed in the vessel in which it is contained. This change of color is due to the action of the oxygen of the air. Some of the sulphide is decomposed into ammonia, water, and sulphur:



The sulphur thus set free combines with the undecomposed ammonium sulphide, forming the compounds  $(\text{NH}_4)_2\text{S}_2$ ,  $(\text{NH}_4)_2\text{S}_3$ , etc., known as *polysulphides*. When as much sulphur as possible has been taken up in this way, any more that may be set free by the action of oxygen is deposited.

A solution containing the polysulphides is called *yellow ammonium sulphide*. It is used to dissolve the sulphides of arsenic, antimony, and tin in analytical operations. (See description of method of analysis, page 316.)

#### PREPARATION OF AMMONIUM SULPHIDE.

*Experiment 148.*—Saturate 25 cc. strong aqueous ammonia with hydrogen sulphide. Add to the saturated solution 25 cc. of the same aqueous ammonia.

**Ammonium Hydrosulphide,  $\text{HNH}_4\text{S}$ .**—As stated above, a solution of this substance is made by passing hydrogen sulphide into a solution of ammonia until no more is taken up.

**Sodium-ammonium Phosphate,  $\text{HNaNH}_4\text{PO}_4 + 4\text{H}_2\text{O}$ .**—This is commonly called *microcosmic salt*, and is much used in the laboratory in blowpipe work. Its value in this kind

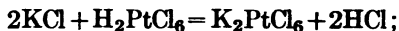
of work depends upon the fact that it is decomposed by heat, yielding sodium metaphosphate:



The metaphosphate at high temperatures combines with the metallic oxides, forming double phosphates, many of which are colored.

**General Characteristics of the Metals of the Alkalies.—**

From what has been said, it will be seen that nearly all the compounds of these metals are soluble in water. Of those mentioned only monosodium carbonate is at all difficultly soluble. There are a few insoluble salts of potassium, those which are chiefly used in analytical operations being the *chloroplatinate*,  $\text{K}_2\text{PtCl}_6$ , which is formed by adding a solution of chlorplatinic acid,  $\text{H}_2\text{PtCl}_6$ , to a solution containing potassium chloride:



and the *fluosilicate*,  $\text{K}_2\text{SiF}_6$ , which is formed when a solution of fluosilicic acid,  $\text{H}_2\text{SiF}_6$ , is added to a solution containing a salt of potassium.

**PRECIPITATION OF POTASSIUM.**

*Experiment 149.*—Add chlorplatinic acid (commonly called platinum chloride) and fluosilicic acid to concentrated solutions of potassium chloride. If in the former case no precipitate is formed, add a little alcohol; potassium chloroplatinate is slightly soluble in water, but is insoluble in dilute alcohol. Potassium fluosilicate is precipitated only from rather concentrated solutions, and even from these, as a rule, only after standing for a while.

**Rare Elements of this Group.**—The elements *lithium*, *cæsium*, and *rubidium* are much rarer than sodium and potassium. Lithium is found in a form of mica known as lepidolite. It is the lightest metal known (see page 305), and its atomic weight, 7, is smaller than that of any other metal.

**Relations between the Atomic Weights of the Members of this Group.**—The relations between the atomic weights of the members of this group are similar to those already noticed between chlorine, bromine, and iodine; sulphur, selenium, and tellurium; and phosphorus, arsenic, and antimony. Thus, we have lithium, 7; sodium, 23; and potassium, 39. The atomic weight of sodium, 23, is the mean of those of lithium, 7, and potassium, 39:

$$\frac{7+39}{2}=23.$$

Similarly, the atomic weight of rubidium, 85, is nearly the mean of those of potassium and cæsium, 133:

$$\frac{39+133}{2}=86.$$

**Flame Reactions and the Spectroscope.**—When a clean piece of platinum wire is held for some time in the flame of a Bunsen burner, it then imparts no color to the flame. If now a small piece of sodium carbonate or any other salt of sodium is put on it, it colors the flame intensely yellow. All sodium compounds have this power, and the chemist makes use of the fact for the purpose of detecting the presence of sodium. Similarly, potassium compounds color the flame violet; lithium compounds color the flame red; and the

other metals of the family also impart characteristic colors to the flame.

#### FLAME REACTIONS.

*Experiment 150.*—Prepare some pieces of platinum wire, 8 to 10 cm. long, with a loop on the end, like those used in blow-pipe work. After thoroughly cleaning them by dipping them in dilute hydrochloric acid and heating in the flame of a Bunsen burner, insert one in a little sodium carbonate, and notice the color it gives to the flame. Try another with potassium carbonate, and, if the substances are available, others with a calcium, barium, and a strontium salt.

While it is an easy matter to recognize potassium alone, or any one of the other metals alone, it is difficult to do so when they are together in the same compound. For example, when sodium and potassium are together, the intense yellow caused by the sodium completely masks the more delicate violet caused by the potassium, so that the latter cannot be seen by the unaided eye. In this particular case the difficulty can be overcome by letting the light from the flame pass through a blue glass, or through a thin vessel of glass containing a solution of indigo. The yellow light is thus cut off, while the violet light passes through and can be recognized. A more general method for detecting the constituents of light is by means of a prism of glass. Lights of different colors, which are produced by ether waves of different lengths, are turned out of their course to different extents when passed through a prism, as is seen when white sunlight is passed through a prism. A narrow beam of white light passing in emerges as a band of various colors, called its *spectrum*. It is thus seen that white light is made up of lights of different colors; or, to

speak in the language of physics, that motion of the light-ether which produces upon the eye the sensation of white light is made up of a number of motions, each of which alone produces upon the eye the sensation of a color. Similarly, the composition of any light can be determined. Every light has its characteristic spectrum. The light given off from any solid heated to a white heat gives a *continuous spectrum*, like that of the sunlight. An incandescent gaseous substance, on the other hand, gives a spectrum made up of separate bands of color, or a *band spectrum*. The light produced by burning sodium, or by introducing a sodium compound in a colorless flame, gives a spectrum consisting of a narrow yellow band. The spectrum of the potassium flame consists essentially of two bands, one red and one violet. Further, these bands always occupy definite positions relatively to one another, so that, in looking through a prism at the light caused by potassium and sodium, the yellow band of sodium is seen in its position, and the two potassium bands in their proper positions. There is therefore no difficulty in detecting these elements when present in the same substance or in the presence of other elements which give charactersitic spectra.

The light emitted by hydrogen shows a bright green line, a bright red line, and a line in the violet. No other substance shows lines in the same positions. If sunlight is allowed to pass through a prism dark lines appear in the exact positions of the colored hydrogen lines. These dark lines are due to the hydrogen in the atmosphere of the sun. The law of Bunsen and Kirchoff is that a gas absorbs the same wave lengths that it emits. White light from

the sun's heated nucleus passing through the hydrogen atmosphere has those wave lengths absorbed which hydrogen emits. Hence the dark lines in the spectrum. Such spectra are called *absorption spectra*. Our knowledge of the presence of terrestrial elements in the sun, stars and nebulae is due to observations of this kind. The sun and stars are incandescent bodies surrounded by a gaseous atmosphere and yield absorption spectra. The nebulae are incandescent gases and yield band spectra.

The instrument used for the purpose of observing the spectra of different lights is called the *spectroscope*.\* It consists essentially of a prism and two small telescopes. Through one of the telescopes the light to be examined is allowed to pass so as to strike the prism properly. The light emerges from the other side of the prism, and is observed through the other telescope, which is provided with lenses for the purpose of magnifying the spectrum. By means of a third telescope, an image of a scale is thrown upon the face of the prism from which the spectrum emerges, and is reflected thence into the observing-tube, together with the spectrum, so that the position of the bands can be accurately determined. By means of the spectroscope it is possible to detect the minutest quantities of some elements, and, since it was devised, several new elements have been discovered through its aid; as, for example, caesium, rubidium, thallium, indium, gallium, and some of the rare gases in the atmosphere.

\* For an account of the spectroscope and its uses, the student should consult some work on physics. The principles involved in its construction and application are physical principles, and cannot properly be taken up in detail in a text-book of chemistry.

**Helium.**—The element *helium* was discovered by the spectroscope in the chromosphere and the protuberances of the sun. Later it was found in a gas given off from certain rare minerals, and it has since been found in the air in minute quantity. It is a very light gas, its specific gravity as compared with air being 0.14. Its atomic weight is 4, which is also its molecular weight. It is as inactive as argon.

## CHAPTER XXI.

### THE CALCIUM GROUP: CALCIUM, BARIUM, STRONTIUM, GLUCINUM.

**General.**—The three elements calcium, barium, and strontium resemble one another very closely. Calcium is much more abundant than either of the other members of the group, while strontium is the least abundant of the three. For the present it will be best to confine our attention to the principal member, calcium.

**Calcium, Ca (At. Wt. 40).**—This element occurs very widely distributed in nature, and in enormous quantities. It is found principally as carbonate,  $\text{CaCO}_3$ , in the form of *limestone*, *marble*, and *chalk*; as sulphate,  $\text{CaSO}_4$ , in the form of *gypsum*; as phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , in *phosphorite*. and *apatite*; as fluoride,  $\text{CaF}_2$ , in *fluor-spar*.

The element is made by heating a mixture of calcium oxide and carbon in an electric furnace.

It is a silver-white, lustrous substance, which in moist air becomes covered with a layer of hydroxide. At ordinary temperatures it decomposes water just as sodium and potassium do. It is one of the most active elements. It is found in solution in most natural waters either as the carbonate or sulphate; and in the organs of plants and animals. Bones contain a large proportion of calcium phosphate; egg-shells and coral contain calcium carbonate.

**Preparation.**—Calcium is made: (1) By heating together



anhydrous calcium iodide and metallic sodium; (2) commercially, by the electrolysis of calcium chloride.

**Properties.**—Calcium is silver-white, hard, and tough. It melts at  $800^{\circ}$ . It is one of the most active elements known, and combines with all the other elements except the inactive gases of the air. It combines with hydrogen to form the hydride  $\text{CaH}_2$ , and burns brilliantly in the air, forming compounds with both oxygen and nitrogen. It decomposes water easily and becomes incandescent if in the form of powder.

**Compounds of Calcium.**—The principal compounds of calcium with which we have to deal are the *chloride*,  $\text{CaCl}_2$ ; the *oxide*, or quicklime,  $\text{CaO}$ ; the *hydroxide*, or slaked lime,  $\text{Ca}(\text{OH})_2$ ; the *carbide*,  $\text{CaC}_2$ ; the *hypochlorite*,  $\text{Ca}(\text{OCl})_2$ ; the *carbonate*,  $\text{CaCO}_3$ ; the *sulphate*,  $\text{CaSO}_4$ ; the *phosphate*,  $\text{Ca}_3(\text{PO}_4)_2$ ; and the *silicate*, in the form of glass.

**Calcium Chloride**,  $\text{CaCl}_2$ .—The property which gives this salt its value is its power to absorb water. It is used as a drying agent. Gases are passed through it for the purpose of drying them, and it is also placed in vessels in which it is necessary that the atmosphere should be dry. It is obtained as a by-product in the preparation of ammonia from ammonium chloride and lime; in the preparation of potassium chlorate from calcium chlorate and potassium chloride (see p. 468); and in the ammonia-soda process.

#### PREPARATION OF CALCIUM CHLORIDE.

*Experiment 151.*—Dissolve 10 to 20 grams of limestone or marble in ordinary hydrochloric acid. Evaporate the solution to dryness. Expose a few pieces of the residue to the air. Does it become moist? In what experiments has calcium chloride been

used, and for what purposes? What would happen if sulphuric acid were added to calcium chloride? Try it. Explain what takes place. Is the residue soluble or insoluble in water?

**Calcium Oxide,  $\text{CaO}$ .**—This is the substance commonly called *lime*, or, to distinguish it from the hydroxide or *slaked lime*, it is called *quicklime*. It is made by heating calcium carbonate, which is thus decomposed into lime and carbon dioxide:



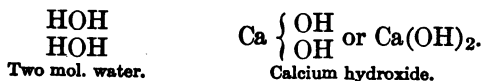
Limekilns are large furnaces in which limestone and other forms of calcium carbonate are heated and converted into lime.

[Why is it dangerous to remain for any length of time in the immediate neighborhood of a limekiln?]

Lime is a white, amorphous, infusible substance. When heated in the flame of the compound blowpipe, it gives out an intense light, as any other infusible substance would under the same circumstances. When exposed to the air it attracts moisture and carbon dioxide and is thus converted into a mixture of the hydroxide and the carbonate. It must hence be protected from the air. Lime that has been converted into the carbonate by exposure to the air is said to be *air-slaked*.

**Calcium Hydroxide,  $\text{CaO}_2\text{H}_2$ , or  $\text{Ca}(\text{OH})_2$ .**—When calcium oxide or quicklime is treated with water, it becomes hot and crumbles to a fine powder. The substance formed in this operation is somewhat soluble in water, the solution being known as *lime-water*. The chemical change that takes place when lime is treated with water has been explained (page 159). It consists in the formation of a compound of the formula  $\text{CaO}_2\text{H}_2$  and known as slaked lime.

and the operation is known as *slaking*. It is believed that just as potassium hydroxide, KOH, is properly regarded as water in the molecule of which one atom of potassium is substituted for an atom of hydrogen, so calcium hydroxide is properly regarded as derived from water by the substitution of an atom of calcium for two atoms of hydrogen in two molecules:



It is difficult to explain exactly why this view is held. It can only be said that it is a conception in harmony with a great many facts, though it does not follow as a necessary consequence from any facts known to us.

#### CALCIUM HYDROXIDE.

*Experiment 152.*—Moisten 40 to 50 grams quicklime with warm water. Soon the mass will begin to crumble, and steam will rise from it, indicating that heat is evolved. Afterwards dilute to 2 or 3 litres and put the whole in a well-stoppered bottle. The undissolved lime will settle to the bottom, and in the course of some hours the solution above will become clear. Carefully pour off some of the clear solution. [What takes place when some of the solution is exposed to the air? when the gases from the lungs are passed through it? when carbon dioxide is passed through it? What takes place when dilute sulphuric acid is added to lime-water? Is calcium sulphate difficultly or easily soluble in water? Has lime-water an alkaline reaction?]

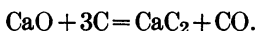
When potassium hydroxide is added to a solution of a salt containing a metal whose hydroxide is insoluble in water, the insoluble hydroxide is precipitated. This was illustrated in Experiments 131 and 132 (page 340). Calcium hydroxide is a soluble hydroxide, and acts in the same way that potassium hydroxide does.

## PRECIPITATION OF METALLIC HYDROXIDES BY LIME-WATER.

*Experiment 153.*—Add a small quantity of dilute solutions of ferric chloride, of copper nitrate, of lead nitrate to separate portions of lime-water contained in test-tubes. Explain the results.

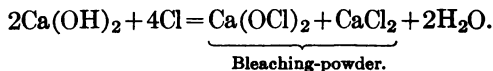
**Uses.**—Lime is extensively used in the arts, generally in the form of the hydroxide. As we have seen, it is used in the preparation of ammonia and of the caustic alkalies, potassium and sodium hydroxides; and of bleaching-powder and potassium chlorate. It is further used in large quantity in the process of tanning for removing the hair from hides; in decomposing fats for making stearin for candles; for purifying illuminating-gas; and especially in the preparation of mortar.

**Calcium Carbide,  $\text{CaC}_2$ .**—This compound is easily formed by heating lime and coke together in the form of powder in an electric furnace, when the reaction represented below takes place:



It is a crystallized substance. With water it gives acetylene and lime. (See Acetylene.)

**Calcium Hypochlorite,  $\text{Ca}(\text{OCl})_2$ ,** has already been referred to under Chlorine, page 128. The form in which chlorine is transported is "bleaching-powder," a compound containing calcium hypochlorite and calcium chloride,  $\text{Ca}(\text{OCl})_2 + \text{CaCl}_2$ , made by treating slaked lime with chlorine:

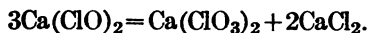


The compound is commonly called "chloride of lime." An objection to the view that calcium chloride is present as such in bleaching-powder is found in the fact that the substance is not deliquescent. This has led to the suggestion that bleaching-powder in the dry form is not a mixture of two compounds as represented above, but that it is rather one compound of the formula  $\text{Ca} < \begin{smallmatrix} \text{Cl} \\ \text{OCl} \end{smallmatrix}$  or  $\text{CaOCl}_2$ . The point is a difficult one to decide, but at present the evidence appears to be in favor of the view that bleaching-powder in the dry form is a single compound of the constitution represented by the formula last given. When treated with water, however, it forms the ions  $\text{Ca}$ ,  $\text{Cl}$ , and  $\text{OCl}$ , which are the same ions that would be formed by dissolving a mixture of calcium chloride and calcium hypochlorite.

**Properties.**—Bleaching-powder is a white substance that has the odor of hypochlorous acid. When treated with an acid it gives up all its chlorine. When exposed to the action of carbon dioxide hypochlorous acid is liberated. Hence this decomposition takes place slowly in the air.

**How Bleaching-powder Acts in Bleaching.**—A solution of bleaching-powder alone is not capable of bleaching except very slowly. If, however, something is added which has the power to decompose it, bleaching takes place, the action being due to the presence of hypochlorous acid and chlorine. As is clear from what was said above, the passage of carbon dioxide through the solution or the addition of an acid would cause it to bleach. So, too, certain salts produce a similar effect. The explanation of this is the instability of the hypochlorites which are formed by the salts added.

**Decomposition of Bleaching-powder by Boiling its Solution.**—When a concentrated solution of bleaching-powder is heated it gives off oxygen, and the salt is converted into the chloride. In dilute solution, however, the hypochlorite is converted into chlorate and chloride:



This fact is taken advantage of, as has been shown, for the purpose of making calcium chlorate, and from this potassium chlorate (see page 363). In contact with certain oxides, as copper oxide, ferric oxide, and with hydroxides, as those of cobalt and nickel, a solution of bleaching-powder readily gives up oxygen when heated.

**Uses.**—The chief application of bleaching-powder is, as its name implies, for bleaching. It is also used as a disinfectant and as an antiseptic, that is, for the purpose of destroying disease germs and of preventing decomposition of organic substances.

**Calcium Carbonate,  $\text{CaCO}_3$ .**—This salt occurs in immense quantities in nature in the well-known forms limestone, calc-spar, marble, and chalk. The variety of calc-spar found in Iceland, and known as Iceland spar, is particularly pure. Calcium carbonate crystallizes in a number of different forms, the most common being rhombohedrons, as seen in ordinary calc-spar. A second variety of crystallized calcium carbonate is aragonite. This is found in nature crystallized in rhombic prisms, and in forms derived from this. When heated, aragonite falls to pieces, the particles being small crystals of the form characteristic of calc-spar. This is a case of dimorphism similar to that

presented by sulphur, which, it will be remembered, crystallizes in two forms, rhombic and monoclinic, the latter of which passes into the former spontaneously. These forms are produced artificially very readily. When calcium carbonate is precipitated from a solution of a calcium salt by adding a soluble carbonate at ordinary temperatures, the precipitate is made up of microscopic crystals which have the same form as calc-spar. If, however, the solution from which the carbonate is precipitated is hot, the salt consists of microscopic crystals of the form of aragonite.

The most abundant form of calcium carbonate is limestone, of which many great mountain-ranges are largely made up. This is a compact form of the compound, which has a gray color, and frequently consists of minute crystals. It is always more or less impure, containing clay and other substances. Limestone which is mixed with a considerable proportion of clay is called *marl*. Many natural waters contain calcium carbonate in solution—probably in the form of the acid carbonate. When such a water evaporates, the carbonate is deposited. It happens in some places that a water charged with the carbonate works its way slowly through the earth and drops from the top of a cave. Under these circumstances there is a gradual deposit of the salt which remains suspended. Such hanging formations of the carbonate are known as *stalactites*. At the same time that part of the liquid which falls to the bottom of the cave forms a projecting mass below the stalactite. Such projecting masses are called *stalagmites*. The formation of stalactites takes place in somewhat the same way as that of icicles.

Much of the calcium carbonate found in nature has its origin in the remains of animals, and fossils are very abundant in it. Chalk consists almost exclusively of the shells of microscopic animals.

**Temporary Hardness.**—When carbon dioxide is passed into a solution of calcium hydroxide, the carbonate is precipitated; and, if the current of gas is continued long enough, the carbonate is redissolved. On heating the solution to boiling, carbon dioxide is given off and the normal carbonate is again precipitated. Natural waters that come in contact with limestone gradually take up more or less of the carbonate, because of the carbon dioxide dissolved in them, and when such a water is boiled, the carbonate is thrown down. A water containing calcium carbonate in solution is called a *hard water*; and, as this kind of hardness is easily removed by boiling, it is called *temporary hardness* in order to distinguish it from a kind which is not removed by boiling, and therefore called *permanent hardness*. Further, temporary hardness is removed by adding lime to the water, when the normal carbonate is formed, which is at once precipitated.

The decomposition of calcium carbonate by heat, forming lime, or calcium oxide, and carbon dioxide, was referred to on page 388.

**Applications.**—Calcium carbonate is used in the arts for a great many purposes, as in the manufacture of glass; as a flux in many important metallurgical operations, as in the reduction of iron from its ores; in the preparation of lime for mortar, etc. As is well known, further, marble



and some of the varieties of limestone are extensively used in building, and large quantities of chalk are also used.

**Calcium Sulphate,  $\text{CaSO}_4$ .**—This compound is very abundant in nature. The principal natural variety is gypsum, which occurs in crystals containing two molecules of water,  $\text{CaSO}_4 + 2\text{H}_2\text{O}$ . The salt of the formula  $\text{CaSO}_4$  also occurs in nature, and is called anhydrite. A granular form of gypsum is called alabaster. Calcium sulphate is difficultly soluble in hot and cold water. When heated to  $100^\circ$ , or a little above, it loses nearly all its water and forms a powder known as plaster of Paris, which has the power of taking up water and forming a solid substance. This process of solidification is known as "setting." Plaster of Paris is very largely used in making casts, on account of its power to harden after having been made into a paste with water. The hardening is a chemical process, and is caused by the combination of water with the salt to form the crystallized variety.

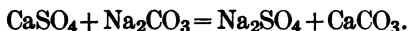
When heated to  $200^\circ$  and higher all the water is given off from gypsum, and the product now combines with water only very slowly, and is of no value for making casts. In general, the higher the temperature to which the gypsum is heated the greater the difficulty with which the product combines with water.

#### PREPARATION OF PLASTER OF PARIS.

*Experiment 154.*—Heat some gypsum to between  $140^\circ$  and  $160^\circ$  in an air-bath. Examine the residue and see whether it will become solid when mixed with a little water so as to form a paste.

**Permanent Hardness.**—Many natural waters contain gypsum in solution. Such waters act in some respects like those which contain calcium carbonate. With soap, for example, they form insoluble compounds. This kind of hardness is not removed by boiling, and it is therefore called *permanent hardness* (see paragraph on "Temporary Hardness," page 394). Magnesium sulphate acts in the same way, producing permanent hardness.

**Action of Soluble Carbonates on Gypsum.**—When calcium sulphate is treated with a solution of a soluble carbonate, it is decomposed, forming calcium carbonate as represented in the equation



This change is effected simply by allowing the two to stand in contact at the ordinary temperature.

#### CONVERSION OF GYPSUM INTO CALCIUM CARBONATE.

*Experiment 155.*—Upon a gram or two of powdered gypsum pour, say, 50 cc. of a moderately strong solution of ammonium carbonate. After a few hours pour off the solution, collect the powder on a filter, wash it thoroughly with water and see whether it has changed to the carbonate. [How can you determine whether ammonium sulphate is in solution or not? Of course, there is still ammonium carbonate present, and this must be taken into account in examining for the sulphate. We usually examine for a sulphate by adding a soluble barium salt, when, if a soluble sulphate is present, barium sulphate is precipitated. In this case, however, the ammonium carbonate would throw down barium carbonate. To prevent this, the ammonium carbonate is decomposed by slowly adding sufficient dilute hydrochloric acid. There will then be present ammonium chloride and sulphate;

and, now, if barium chloride or any other soluble barium salt is added, barium sulphate will be precipitated.]

**Uses.**—Besides being used for making casts, calcined gypsum is used in surgery for making plaster-of-Paris bandages and as a fertilizer. Its action as a fertilizer is thought by some to be due to the fact that it has the power to hold ammonia and ammonium carbonate in combination, and thus to make them available for the plants. It has been shown that it in some way facilitates the process of nitrification, and perhaps it is in consequence of this that it aids plant-growth.

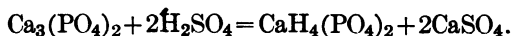
**Calcium Phosphates.**—There are three phosphates of calcium: (1) the *normal phosphate*,  $\text{Ca}_3(\text{PO}_4)_2$ ; (2) the *secondary phosphate*,  $\text{CaHPO}_4$ ; and (3) the *primary phosphate*,  $\text{CaH}_2(\text{PO}_4)_2$ .

*Normal calcium phosphate* is found in nature in large quantity as *phosphorite*, and in combination with calcium fluoride or chloride as *apatite*. It is, further, the principal inorganic constituent of bones, forming 85 per cent of bone-ash.

**Calcium Phosphate Essential to Plant-growth.**—Calcium phosphate is found everywhere in the soil, and is taken up by the plants for whose growth it is essential. That it is also essential to the life of animals is obvious from the fact that the bones consist so largely of it. The phosphate required for the building up of bones is taken into the system with the food. From these statements it is clear that calcium phosphate is of fundamental importance, and that a fertile soil must either contain this salt or something from which it can be formed. Now, when a crop is raised on a given area, a certain amount of the phosphate con-

tained in it is withdrawn. If the plants were allowed to decay where they grow, the phosphate would be returned and the soil would continue fertile; but in cultivated land this is not the case. The crops are removed, and with them the calcium phosphate, and the soil therefore becomes exhausted. If the substances removed are used as food, some of the phosphate is found in the excrement of the animals; and, if the excrement is put on the soil, this is again rendered fertile.

**Artificial Fertilizers.**—There are, however, other sources of calcium phosphate, and some of these are utilized extensively in the preparation of artificial fertilizers. The natural form of the phosphate, as that in bone-ash, in phosphorite, and in guano, is mainly the normal or neutral phosphate. This is insoluble in water, and is therefore taken up by the plants with difficulty. To make it quickly available, it must be converted into a soluble phosphate. This is done by treating it with sulphuric acid in order to effect the reaction represented in this equation:

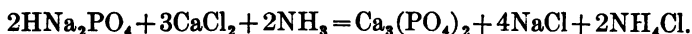


The primary phosphate thus formed is soluble in water, and is of great value as a fertilizer. The mixture of the soluble phosphate and of calcium sulphate is known as "superphosphate of lime." The sulphate, as we have seen, is also of value as a fertilizer. The value of superphosphates depends mostly upon the amount of soluble phosphate contained in them; and in dealing with them it is customary to state how much "soluble" and how much

"insoluble phosphoric acid" they contain. When a superphosphate is allowed to stand for a time, some of the soluble primary phosphate is converted into insoluble phosphates by contact with basic hydroxides and water. This is known as the process of "reversion," and that part of the phosphoric acid which is contained in the insoluble phosphate is spoken of as "reverted phosphoric acid."

**Formation of Calcium Phosphate by Precipitation.—**

Normal calcium phosphate, as has been stated, is insoluble in water, and is formed when a soluble normal phosphate is added to a solution of a calcium salt. It is also formed when disodium phosphate and ammonia are added to a solution of a calcium salt, thus:



**PRECIPITATION OF CALCIUM PHOSPHATE.**

*Experiment 156.*—To a solution of calcium chloride in a test-tube add disodium phosphate and ammonia. The precipitate will dissolve in hydrochloric or nitric acid.

**Primary Calcium Phosphate,  $\text{CaH}_4(\text{PO}_4)_2$ ,** is commonly called the acid phosphate of calcium. It is formed when ordinary insoluble calcium phosphate is treated with concentrated sulphuric acid, and is contained in the so-called superphosphates.

**Production of Phosphate Rock for Fertilizers.**—In the year 1905 the United States produced 1,978,345 tons, Algeria 334,784, Tunis 521,731, France 476,720, Belgium 193,304, and other countries for which the statistics are not yet available produced smaller quantities.

**Fertilizers.**—The most important constituents of all plant foods are nitrogen, phosphoric acid, potassium salts and lime. Nitrogen is obtained by the use of animal manure; in commercial fertilizers Chili saltpetre, ammonium sulphate, guano, and the nitrogenous by-products from the packing houses and the menhaden oil industry are the chief sources, to which must now be added calcium nitrate from the Birkeland-Eyde process (p. 179), and calcium cyanamide from the Frank process (p. 406).

Phosphoric acid is applied as ground bone and as superphosphate which is made from phosphate rock and from the phosphatic slag of the Thomas-Gilchrist basic steel process (which see).

Lime occurs in the phosphates, and gypsum and slaked lime are also used.

Potassium is applied as sulphate derived from the Stassfurt deposits.

It should be noted that ammonia, calcium, and potassium are not applied as chlorides, chlorine-ion being apparently injurious to land plants.

**Action of Acid and Basic Fertilizers on Soil.**—Fertilizers having an acid reaction with litmus render the soil porous, giving ready access of air and water to the plant roots. Fertilizers having a basic reaction with litmus have the opposite effect. Hence, independently of the food constituents, an acid fertilizer is better for a dense clay soil, and a basic fertilizer is better for a porous sandy soil.

**Calcium Silicate,  $\text{CaSiO}_3$ ,** occurs in nature as the mineral wollastonite, and, in combination with other silicates,

in a large number of minerals, as garnet, mica, etc. It is formed when a solution of sodium silicate is added to a solution of calcium chloride, and when a mixture of calcium carbonate and quartz is heated to fusion.

**Glass.**—By the name glass is meant an uncrystallized, transparent or translucent mixture of silicates one of which is always that of an alkali metal (see page 353). Ordinary glass is a silicate of calcium and sodium made by melting sand (silicon dioxide, silica,  $\text{SiO}_2$ ) with lime and sodium carbonate (soda) or sodium sulphate. Instead of calcium carbonate, lead oxide may be used; and instead of sodium carbonate, potassium carbonate. The properties of the glass vary according to the materials used in its manufacture.

*Ordinary window-glass* is a sodium-calcium glass. The purer the calcium carbonate and silica, the better the quality of the glass. This glass is comparatively easily acted upon by chemical substances, and is therefore not adapted to the preparation of vessels that are to be used to hold acids and other chemically active substances. It answers, however, very well for windows. The difference between ordinary window-glass and plate glass is essentially that the former is blown and then cut into pieces, while the latter, when in the molten condition, is run into flat moulds and there allowed to solidify.

*Bohemian glass* is made with potassium carbonate. If pure carbonate is used, as well as pure calcium carbonate and silica, a very beautiful glass is the result. It is characterized by great hardness, by its difficult fusibility, and by its resistance to the action of chemical substances. It

is particularly well adapted to the manufacture of vessels for use in chemical laboratories.

*Flint-glass* is made by melting together lead oxide, potassium carbonate, and silicon dioxide. It is characterized by its power to refract light, its high specific gravity, its low melting-point, and the ease with which it is acted upon by reagents. Owing to its high refractive power, it is largely used in the manufacture of lenses for optical instruments.

*Strass* is a variety of lead-glass that is particularly rich in lead. Its refracting power is so great that it is used in the manufacture of artificial gems.

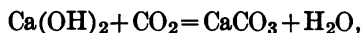
Colors are given to glass by putting into the fused mass small quantities of various substances. Thus, a cobalt compound makes glass blue; copper and chromium make it green; one of the oxides of copper makes it red; uranium gives it a yellow color, etc. The most common variety of glass is that used in the manufacture of ordinary bottles. It is generally green to black, and sometimes brown. In its manufacture impure materials are used, chiefly ordinary sand, limestone, sodium sulphate, common salt, clay, etc.

Glass which has been suddenly cooled is very brittle and breaks into small pieces when scratched or slightly broken in any way. This is shown by the so-called Prince Rupert's drops, which are made by dropping glass, in the molten condition, into water. When the end of such a drop is broken off, the entire mass is completely shattered into minute pieces. It is clear from this that, in the manufacture of glass objects, care must be taken not to cool them suddenly. In fact they are cooled very slowly, the



process being known as *annealing*. For this purpose they are placed in furnaces the temperature of which is but little below that of fusion, and are kept there for some time, the heat being gradually lowered. If red-hot glass is introduced into heated oil or paraffin, and allowed to cool, it is found to be extremely hard and elastic. The glass of De la Bastie is made in this way. Vessels made of it can be thrown about upon hard objects without breaking, but sometimes a slight scratch will cause the glass to fly to pieces, as the Rupert's drops do.

**Mortar.**—Mortar is made of slaked lime and sand. When this mixture is exposed to the air, carbonate of calcium is slowly formed, and the mass becomes extremely hard. The water contained in the mortar soon passes off, but nevertheless freshly-plastered rooms remain moist for a considerable time. This is due to the fact that a reaction is constantly taking place between the carbon dioxide and calcium hydroxide by which calcium carbonate and water are formed,



and it is the water thus liberated that keeps the air moist. The complete conversion of the lime into carbonate requires a very long time, because the carbonate which is formed on the surface protects the lime in the interior to some extent.

It is generally regarded as unhealthy to live in rooms with freshly-plastered walls, because the air is constantly kept moist in consequence of the reaction above mentioned. It is, however, difficult to see why the presence of a little extra moisture in the air should be unhealthy; and, if there

is any danger from freshly-plastered walls, it seems probable that the cause must be sought elsewhere. It is possible that the constant presence of moisture in the pores of the walls interferes with the important process of diffusion, and that, therefore, when the room is closed this natural method of ventilation cannot come into play.

**Cements.**—When a limestone that contains magnesium carbonate and aluminium silicate in considerable quantities is heated for the preparation of lime, the product does not act with water as calcium oxide does, and this lime is not adapted to the preparation of ordinary mortar. On the other hand, it gradually becomes solid, in contact with water, for reasons which are not known. Such substances are known as *cements*, or *hydraulic cements*.

**Portland Cement.**—Far more important than the natural cement is the artificial or Portland cement, which is made by heating together lime and aluminium silicate, and powdering the fused product. It has been found recently that blast-furnace slags fused with lime and sand in suitable proportions form an equally good cement.

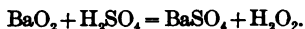
**Concrete.**—When broken rock and cement are mixed, and the mass allowed to harden, a material as durable as the best stone results. This is called concrete. It has been used for a long time for building under water, and is now coming into general use as house-building material. The manufacture of cement is increasing rapidly, chiefly to supply the demand for concrete. In the year 1904, 3,000,000 tons of cement was produced in the United States, 2,500,000 in Germany, 2,500,000 in England and 2,240,000 in other countries, giving a total of 10,240,000 tons.

**Calcium Sulphide**,  $\text{CaS}$ , is formed by heating calcium sulphate with charcoal. It is remarkable for the reason that it is phosphorescent. After having been exposed to sunlight, it continues to give light for some time afterward. This and the similar compound, barium sulphide, are used to some extent in the preparation of luminous objects, such as match-boxes, clock-faces, plates for house-numbers, etc.

**Barium and Strontium.**—The compounds of barium and strontium closely resemble those of calcium. Barium forms an oxide,  $\text{BaO}$ , corresponding to lime, and also another one known as barium dioxide,  $\text{BaO}_2$ .\* This is formed by passing oxygen or air over barium oxide heated to a dull red heat. At a higher temperature it gives off the oxygen. These facts have been utilized for the purpose of extracting oxygen from the air.

Barium oxide is converted into the hydroxide,  $\text{Ba}(\text{OH})_2$ , when treated with water. This hydroxide is soluble in water, the solution being known as *baryta-water*.

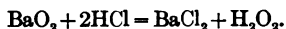
\* This compound has already been referred to (see pp. 76, 107) in describing the preparation of hydrogen dioxide,  $\text{H}_2\text{O}_2$ . When it is treated with sulphuric acid this reaction takes place:



When barium oxide,  $\text{BaO}$ , is treated with sulphuric acid this reaction takes place:

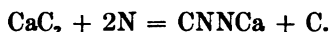


When barium dioxide is treated with hydrochloric acid, hydrogen dioxide is also formed thus:



[Compare this with the action that takes place when hydrochloric acid acts upon manganese dioxide.]

**Calcium Cyanamide**,  $\text{CN}_2\text{Ca}$ , is made by Frank's process by conducting nitrogen (obtained from liquid air) over heated calcium carbide in an electric furnace:



The substance is the calcium salt of cyanamide,  $\text{CNNH}_2$ . It is used as a fertilizer. In contact with the soil its nitrogen passes into the forms of ammonia and nitrates.

**Barium Sulphate**,  $\text{BaSO}_4$ .—This occurs in nature as barite, or heavy spar, and is precipitated when a soluble sulphate or sulphuric acid is added to a solution of a barium salt. It is insoluble in water. When freshly precipitated, it is easily soluble in concentrated sulphuric acid. It is artificially prepared for use as a pigment and is known as *permanent white*. On account of its insolubility it is much used in chemical analysis for the purpose of detecting and estimating sulphuric acid.

*Strontium hydroxide* has the singular property of uniting with sugar, forming difficultly soluble crystalline compounds. It is therefore used for extracting the remaining beet sugar from molasses. The compound is decomposed by carbon dioxide into strontium carbonate and sugar. This is the chief use of strontium compounds.

*Strontium nitrate*,  $\text{Sr}(\text{NO}_3)_2$ , is made in considerable quantity for the purpose of preparing a mixture which, when burned, gives a red light (red-fire, Bengal-fire). It is easily made by dissolving strontianite or strontium carbonate in nitric acid.

**Flame Reactions.**—Calcium compounds color the flame reddish yellow; strontium compounds, intense red; and barium compounds, yellowish green.

**Relations between the Atomic Weights of the Members of this Group.**—Between the atomic weights of calcium, strontium, and barium there exists the same relation as that with which we are already familiar in other groups. The atomic weight of calcium is 40; of strontium, 87; and of barium, 137:

$$\frac{40 + 137}{20} = 88.5.$$

## CHAPTER XXII.

### THE MAGNESIUM GROUP. MAGNESIUM, ZINC, CADMIUM.

OF the three members of this group, magnesium and zinc are by far the most common.

**Magnesium, Mg** (At. Wt. 24).—Magnesium occurs very widely distributed in nature, and in considerable quantities. Among the important magnesium minerals are *carnallite*,  $\text{MgCl}_2 \cdot \text{KCl} + 6\text{H}_2\text{O}$ , or  $\text{MgKCl}_3 + 6\text{H}_2\text{O}$ ; *magnesite*, which is the carbonate,  $\text{MgCO}_3$ ; *dolomite*, a double carbonate of magnesium and calcium; *soapstone*, *serpentine*, and *meerschaum*, which is essentially a silicate of magnesium. Further, there are many silicates that contain magnesium, among them being *asbestos* and *hornblende*. The metal is also found in solution in many spring-waters in the form of the sulphate, or Epsom salt.

**Manufacture.**—It is prepared by electrolysis of dehydrated carnallite,  $\text{MgKCl}_3$ . This is melted in an iron crucible. One pole of the battery is a piece of carbon, the other is the crucible itself.

**Properties.**—It is a silver-white metal with a high lustre. In the air it changes only slowly, but gradually becomes

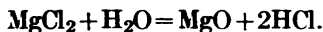
covered with a layer of the oxide. When heated above its melting-point in the air it burns with a bright flame, forming the white oxide and some nitride,  $\text{Mg}_3\text{N}_2$ . The light of the flame is very efficient in producing certain chemical changes, such as the combination of hydrogen and chlorine. Its action upon silver salts is illustrated in photography (see Applications in next paragraph). At ordinary temperatures magnesium does not decompose water; at  $100^\circ$  it decomposes it slowly. [Note the marked difference in this respect between magnesium and the alkali metals and calcium.]

**Applications.**—The principal use to which magnesium is put is for producing a bright light, as for photographing in spaces to which the sunlight does not have access, and for signalling. The so-called “flash-light” is produced by burning magnesium powder. It is also used to some extent as an ingredient of materials employed in making fireworks.

**Compounds of Magnesium.**—The chief compounds of magnesium are the *oxide*,  $\text{MgO}$ , called *magnesia*; the *sulphate*,  $\text{MgSO}_4 + 7\text{H}_2\text{O}$ , commonly called Epsom salt; the *carbonate*,  $\text{MgCO}_3$ ; the *silicates*; and the *chloride*,  $\text{MgCl}_2$ .

**Magnesium Oxide,  $\text{MgO}$ .**—This compound is commonly called *magnesia*. A fine white variety made by heating precipitated magnesium carbonate is called *magnesia usta*. Water acts upon it slowly and converts it into magnesium hydroxide,  $\text{Mg}(\text{OH})_2$ , which is very difficultly soluble in water. [What difference is there between magnesium and calcium in this respect?]

**Magnesium chloride**,  $\text{MgCl}_2$ , is of special interest for the reason that it is the compound from which the metal magnesium was first made. It is prepared by dissolving the carbonate in hydrochloric acid. On evaporating this solution to the proper concentration, crystals of magnesium chloride containing water of crystallization,  $\text{MgCl}_2 + 6\text{H}_2\text{O}$ , are deposited. When this compound is heated for the purpose of drying it, the larger part of it undergoes decomposition, thus:



The same thing takes place to some extent on heating calcium chloride with water, so that fused calcium chloride is always slightly alkaline in consequence of the presence of lime, or calcium oxide.

Dry magnesium chloride is prepared by adding ammonium chloride to its solution and evaporating to dryness. A double chloride of the composition,  $\text{MgCl}_2 \cdot \text{NH}_4\text{Cl}$ , is formed which can be evaporated to complete dryness without decomposition. When perfectly dry this double salt breaks down at a high temperature into ammonium chloride and magnesium chloride. The ammonium chloride is volatilized, and the magnesium chloride remains behind.

**Magnesium Sulphate**,  $\text{MgSO}_4$ .—The mineral kieserite, which occurs at Stassfurt, has the composition  $\text{MgSO}_4 + \text{H}_2\text{O}$ . The salt  $\text{MgSO}_4 + 7\text{H}_2\text{O}$  also occurs in nature. It is this variety which is generally obtained when a solution of magnesium sulphate is evaporated to crystallization. Its water solution has a bitter, salty taste.



## PREPARATION OF MAGNESIUM SULPHATE.

*Experiment 157.*—Make some magnesium sulphate by dissolving magnesite (say 20 grams) in dilute sulphuric acid, filtering and evaporating to crystallization. Pour off the mother-liquor, and dry the crystals by laying them on several sheets of filter-paper.

**Uses.**—Magnesium sulphate finds extensive application. It is used in medicine and is known as Epsom salt, as it is contained in the water of Epsom springs. It is used, further, in the manufacture of sodium sulphate and potassium sulphate, and as a fertilizer in place of gypsum. Its chief use is as a dressing for cotton goods.

**Zinc, Zn (At. Wt. 65).**—Zinc, in almost all its compounds, closely resembles magnesium. It occurs in nature in combination principally as the carbonate, or *smithsonite*,  $\text{ZnCO}_3$ ; as the sulphide, or *sphalerite*,  $\text{ZnS}$ ; and as the silicate,  $\text{Zn}_2\text{SiO}_4$ . Among other compounds of zinc found in nature are *gahnite*,  $\text{Zn(AlO}_2)_2$ , and *franklinite*, which contains the compound  $\text{Zn(FeO}_2)_2$ , together with the analogous compound of iron,  $\text{Fe(FeO}_2)_2$ .

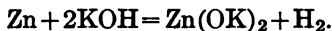
**Metallurgy.**—The metallurgy of zinc is much simpler than that of magnesium, for the reason that the ores are easily converted into the oxide by roasting, and the oxide is easily reduced by heating it with charcoal. Owing to the volatility of the metal the vessels in which the reduction is effected must be so constructed as to facilitate the condensation of the vapor. The vessels used are either earthenware muffles or tubes, open at one end and connected with iron receivers. At first the zinc vapor is condensed in the form of a fine dust, as in the case of sulphur.

This forms the commercial product called *zinc dust*. It always contains zinc oxide. Afterwards the zinc condenses to the form of a liquid, and this is cast in plates. The zinc thus obtained is not pure, but contains lead and iron, and sometimes arsenic and cadmium. It is called *spelter*. By repeated distillation it can be obtained pure. When distilled under diminished pressure, it is deposited in beautiful lustrous crystals, the forms of which are extremely complicated.

Pure zinc is obtained by the electrolysis of solutions of zinc chloride.

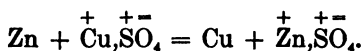
**Properties.**—Zinc has a bluish-white color and a high lustre. The crystals above referred to, which are perfectly pure zinc, have a brilliant lustre and do not change in the air. At different temperatures zinc has markedly different properties. At ordinary temperatures it is quite brittle; at 100°–150° it can be rolled out in sheets, but above 200° it becomes brittle again. It melts at 433°, and boils at 1040°. When heated in the air it takes fire, and burns with a bluish flame, forming zinc oxide. This can be shown by means of the oxyhydrogen blowpipe. In dry air it does not change. Ordinary zinc dissolves in all the common acids, usually with evolution of hydrogen. In the case of nitric acid, however, the acid is to some extent reduced to ammonia. The purer the zinc the less readily is it acted upon by sulphuric acid, and the pure crystals above referred to are scarcely acted upon at all by this acid. Zinc also dissolves in the caustic alkalies, forming zincates. Pure zinc can be made to act upon sulphuric acid by adding a few drops of platinum chloride or of a solution of copper sulphate.

**Applications.**—Zinc is extensively used as sheet-zinc, in making galvanic batteries, for galvanizing iron, etc. Zinc dust is a very efficient reducing agent, either in alkaline or in acid solution. With caustic alkalies—as, for example, with potassium hydroxide—it gives hydrogen and a zincate:



With sulphuric acid also it gives hydrogen readily. Zinc is used in the preparation of important alloys.

**Primary Cells.**—To produce a current of electricity by chemical action the chemical energy of the substances interacting is transformed into electrical energy. If a strip of zinc is placed in a solution of copper sulphate, this reaction occurs:



Zinc dissolves and copper is precipitated; the copper ion gives up its electric charge to the zinc. A current of electricity is not generated because the changes take place in the solution, so that it is not possible to collect and control the electric energy.

In the Daniell cell this is made possible by keeping the solutions separate, but allowing the ions to pass from pole to pole. Fig. 52

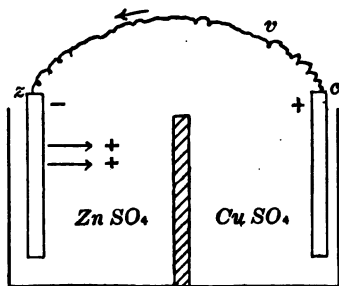


FIG. 52

shows this cell diagrammatically.

As represented, the cell is a vessel divided into two parts by a porous clay partition. The vessel on the left of the partition contains a solution of zinc sulphate into which dips a bar of zinc, Z. The space to the right of the partition contains a solution of copper sulphate and a bar of copper dips into this. A wire connects the copper and zinc bars. Metallic copper from the copper sulphate is deposited on C, while simultaneously zinc dissolves from the surface of Z. At the same time a current of electricity passes from C to Z as indicated by the arrow. As the positive zinc ions leave the surface of the pole Z, this becomes negatively charged from the loss of positive ions. As metallic copper is deposited on the surface of the pole C, it becomes positively charged from the discharge of the positive copper ions. The current passes from + to - through the wire, and carried by the zinc ions passes from - to + through the liquids and through the diaphragm or partition.

Similar cells may be made, in which instead of zinc and copper other metals in solutions of their salts are used; and it is always found that one of the metals is reduced from its salt, while the other dissolves and is ionized. Which of the two will be precipitated and which ionized can be ascertained beforehand by dipping a strip of each in a solution of a salt of the other. One of the two metals will precipitate the other from the solution of its salt. The precipitating metal will be the anode in the cell, the metal precipitated the cathode. A given metal may act as precipitating and as precipitated metal; iron, for example, is precipitated by zinc but precipitates copper

All the metals can be arranged in a series so that every metal precipitates all the metals following it in the series from their salt-solutions, and is precipitated by all the preceding metals of the series.

In the cell the *amount of electromotive force* (see p. 413), produced will vary according to the metals and electrolytes used in the cells, although reactions between equivalent amounts of the metals and electrolytes as stated in Faraday's law give the same *amounts of electricity*. If cells of different metals and their salts are used, and the difference in potential measured by an instrument called a voltmeter introduced into the circuit at *v*, Fig. 56, values can be found for each metal which are given in the table below, which gives the difference in potential in volts for the metals in normal solutions. The signs + and - indicate the nature of the charge of the solution:

Magnesium	+ 1.24	Volts.	Lead	- 0.10	Volts.
Aluminium	+ 1.03	"	Copper	- 0.59	"
Zinc	+ 0.51	"	Mercury	- 1.03	"
Cadmium	+ 0.16	"	Silver	- 1.06	"
Iron	+ 0.09	"			

It will be seen that a zinc-cadmium cell gives + 0.51 minus + 0.16 = 0.35 volts. While a zinc-copper cell gives + 0.51 minus - 0.59 = 1.10 volts and a zinc-silver cell gives + 0.51 minus - 1.06 = 1.57 volts.

**Alloys.**—Iron covered with a layer of zinc is known as *galvanized iron*. Zinc is a constituent of *brass*. It combines readily with mercury to form zinc amalgam, and this fact is taken advantage of for the purpose of preserv-

ing the zinc plates in galvanic batteries. Zinc plates covered with a layer of the amalgam are acted upon much more slowly than zinc itself. The amalgamation is effected by cleaning the zinc, dipping it in dilute sulphuric acid, and rubbing mercury over the surface with a brush or a piece of cloth.

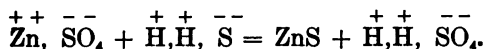
**Zinc oxide**,  $\text{ZnO}$ , is obtained as *Flores zinci* by burning zinc, and by heating the carbonate or nitrate of zinc. It turns yellow when heated, but on cooling becomes white again.

#### BURNING OF ZINC.

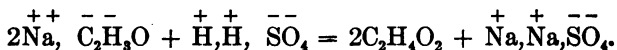
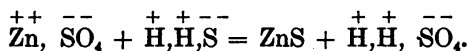
*Experiment 158.*—Heat a small piece of zinc on charcoal in the oxidizing flame of the blowpipe. The white fumes of zinc oxide (philosopher's wool) will be seen, and the charcoal will be covered with a film which is yellow while hot, but becomes white on cooling. [What element gives a film which is white both when hot and when cold?]

Zinc oxide is used as a constituent of paint under the name of *zinc white*.

**Zinc Sulphide**,  $\text{ZnS}$ .—This compound occurs in nature, and is known as zinc blende. The mineral always contains a sulphide of iron, and also a small quantity of cadmium sulphide. When hydrogen sulphide is passed into a solution of a zinc salt only a part of the zinc is thrown down as the sulphide, if the salt used is one of a strong acid, like sulphuric, nitric, or hydrochloric acid. The reason of this is that the sulphide is soluble in these acids, even when they are quite dilute. In the reaction the acid is set free and ionized, and although some sulphide is thrown down, the action soon stops:

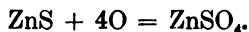


If the acetate of zinc is used the precipitation is complete, because dilute acetic acid does not dissolve zinc sulphide, or because acetic acid is only slightly dissociated, and therefore the disturbing hydrogen ions are not present. If sodium or potassium acetate is added to a solution of a neutral salt of zinc, hydrogen sulphide precipitates all the zinc, for the reason that the ions of the strong acid that are first formed react with the acetate and form the ions of the corresponding salt and also acetic acid, which exists in the solution largely in undissociated condition. Thus the hydrogen ions are eliminated, and the zinc sulphide is not dissolved:

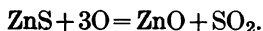


The sulphide is, further, completely precipitated by soluble sulphides, as potassium and ammonium sulphides. Obtained by precipitation, zinc sulphide is a white amorphous substance.

**Zinc sulphate**,  $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ , is commonly called white vitriol. [In what experiments has zinc sulphate been obtained? (see Exps. 29, 30, pages 49, 52.)] It is obtained on the large scale by heating zinc sulphide in contact with the air. Under these circumstances, the sulphide is oxidized:



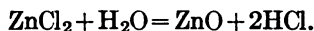
This operation is known as *roasting*, by which term is meant any operation that involves heating an ore to a high temperature, but not high enough to melt the ore or the products formed, so that the air has free access to it. By roasting zinc sulphide at a higher temperature it is converted into zinc oxide:



Zinc sulphate is also formed in large quantities in galvanic batteries and in the preparation of hydrogen.

Zinc sulphate is used as a disinfectant, in medicine, and to some extent as a preservative for hides and timber.

**Zinc chloride**,  $\text{ZnCl}_2$ , is obtained by evaporating a water solution of the substance and distilling the residue. It is an oily liquid which has a very strong affinity for water. On evaporating a water solution a part of the chloride undergoes decomposition, just as magnesium chloride does, forming the oxide:



**Some Insoluble Compounds of Zinc.**—The hydroxide, sulphide, carbonate, and phosphate of zinc are insoluble in water.

#### FORMATION OF INSOLUBLE COMPOUNDS OF ZINC.

*Experiment 159.*—Produce the insoluble compounds just mentioned and express the reactions by means of equations. The phosphate of zinc precipitated by ordinary sodium phosphate is the normal phosphate,  $\text{Zn}_3(\text{PO}_4)_2$ .

[What happens on bringing together solutions of sodium car-



bonate and zinc sulphate? ammonia and zinc chloride? barium chloride and zinc sulphate? lime-water and zinc sulphate? What color has zinc sulphide? Is it thrown down when the solution contains dilute hydrochloric acid? Try it.]

**Cadmium**, Cd (At. Wt. 111.)—This metal is found in nature in combination in some ores of zinc. Its sulphide is yellow and is used as a constituent of yellow paints.

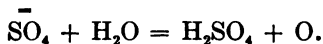
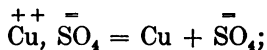
## CHAPTER XXIII.

### THE COPPER GROUP: COPPER, MERCURY, SILVER

**Copper**, Cu (At. Wt. 63.5).—Copper occurs in nature in the uncombined or native state in large quantities in the neighborhood of Lake Superior in the United States, and in China, Japan, Siberia, and Sweden. It also occurs in combination with oxygen as *ruby copper*, which is the oxide  $\text{Cu}_2\text{O}$ ; with sulphur as *chalcocite*,  $\text{Cu}_2\text{S}$ ; and with sulphur and iron in *copper pyrites*,  $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ .

**Metallurgy**.—It is obtained from the oxide by heating it with charcoal. [This reduction has been illustrated under the head of Carbon (see Experiment 87, page 221).] It is also obtained from the sulphides. The chemical changes involved are comparatively complicated. The copper obtained in this way contains impurities the nature of which depends upon the character of the ore used.

Pure copper is now made by the electrolysis of a solution of copper sulphate, a sheet of pure copper being the cathode and a block of impure copper the anode:



The sulphuric acid attacks the anode, dissolving copper

and thus constantly regenerating the solution of copper sulphate. Impurities in the copper, including gold and silver, are deposited at the bottom of the tanks. From this deposit—the “anode mud”—gold and silver are obtained. Electrolytic (or pure) copper conducts electricity twice as well as ordinary copper.

**Properties.**—Copper is a hard metal, of a reddish color and metallic lustre. It does not change in dry air, but in moist air it gradually becomes covered with a green layer of a basic carbonate. It melts at  $1084^{\circ}$  and boils at  $1500^{\circ}$ . It is very malleable and tenacious. Hence its use for wire for conducting electric currents. Weight for weight aluminium offers less resistance to the passage of the current than copper, and aluminium is the cheaper metal, but the greater tenacity of copper makes it cheaper to use copper wires. It decomposes water only at bright-red heat. When heated in the air to a comparatively high temperature it becomes covered with a layer of cupric oxide; at a lower temperature cuprous oxide is formed. Nitric acid dissolves it, copper nitrate,  $\text{Cu}(\text{NO}_3)_2$ , being formed, and oxides of nitrogen evolved [explain the reaction (see page 165)]; hydrochloric acid does not act upon it; sulphuric acid acts when heated with the metal, the sulphate,  $\text{CuSO}_4$ , being formed and sulphur dioxide given off [explain the reaction (see page 294)]. Copper does not decompose water, even when steam is passed over the metal heated to red heat. [Compare with the conduct of the members of the potassium, calcium, and magnesium groups.]

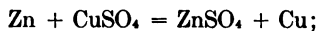
Dilute acids in general do not act upon it unless the air has access to it. This fact is of importance in connection

with the use of copper vessels in culinary operations. Substances containing vegetable acids can be boiled in bright copper vessels with impunity, for the water-vapor prevents access of the air, but, on cooling, the air is admitted, and then action may take place, causing solution of some of the copper, which is objectionable.

**Precipitation of Copper.**—Copper is precipitated from solutions of its salts by zinc, iron, and some other metals, and by an electric current.

#### DECOMPOSITION OF COPPER SULPHATE BY ZINC.

*Experiment 160.*—In a neutral solution of copper sulphate hang a strip of zinc. The zinc will become covered with a layer of copper, and zinc will pass into solution as zinc sulphate. The zinc displaces the copper in this case, as it displaces hydrogen from sulphuric acid:



**Applications.**—As is well known, copper is used very extensively for a variety of purposes, among which the following may be mentioned: for electrical apparatus, coins, copper vessels, roofs, for covering the bottoms of ships, etc. It is also used in copper-plating; and in the preparation of a number of valuable alloys, such as brass, bronze, gun-metal, bell-metal, etc.

The demand for copper has increased enormously within recent years on account of its use for electrical dynamos, cables and wires, and the increasing use of copper salts as germicides. The total production of copper in 1906 was 798,487 tons, of which the United States produced 458,903, Mexico 67,900, Spain 52,528.

**Alloys.**—*Brass* is a mixture of about one part of zinc and two parts of copper; these proportions may, however, be varied between quite wide limits. There is a variety of brass containing equal parts of zinc and copper, and another containing one part of zinc and five parts of copper. *Pinchbeck* is made by combining two parts of copper and one of brass.

*Bronze* consists of copper, zinc, and tin. The proportion of copper varies from 65 to 84 per cent; that of zinc from 31.5 to 11 per cent; and that of tin from 2.5 to 4 per cent. When exposed to the air bronze becomes covered with a green coating of basic copper carbonate, which protects it from further action. This coating is now often produced artificially by a variety of methods, as by washing the surface with a solution of salts and acids.

*Gun-metal* consists generally of copper and tin in the proportion of 11 parts of tin and 100 parts of copper.

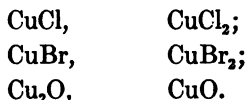
*Bell-metal* contains a larger proportion (from 20 to 25 per cent) of tin than gun-metal does.

*Alloys with aluminium* containing aluminium and copper in widely different proportions are made. That with 3 per cent of copper has a whiter color than aluminium, the color being more like that of silver. On the other hand, an alloy of copper with 5 to 10 per cent of aluminium has a color resembling that of gold. This, which is known as aluminium bronze, is very hard and elastic, and is not easily acted upon by chemical reagents. It is now used to a considerable extent in the manufacture of ornamental and useful articles.

*German silver* is an alloy consisting of copper, zinc, and nickel.

**Compounds of Copper.**—Among the more common compounds of copper are the *oxides*  $\text{Cu}_2\text{O}$  and  $\text{CuO}$ ; the *sulphate*,  $\text{CuSO}_4$ ; the *carbonate*; and the *sulphide*,  $\text{CuS}$ .

**Copper Forms Two Series of Compounds.**—Copper has the power to form two series of compounds, of which the following are examples:



Those compounds which are of the first order, corresponding to the chloride  $\text{CuCl}$ , are called *cuprous compounds*. Thus,  $\text{CuCl}$  is *cuprous chloride*;  $\text{Cu}_2\text{O}$ , *cuprous oxide*, etc. On the other hand, compounds of the second order are called *cupric compounds*. Thus,  $\text{CuCl}_2$  is *cupric chloride*;  $\text{CuO}$ , *cupric oxide*, etc. It has been suggested that perhaps the formulas of the simpler cuprous compounds like  $\text{CuCl}$ , etc., should be doubled, and written  $\text{Cu}_2\text{Cl}_2$ ,  $\text{Cu}_2\text{Br}_2$ , etc. This suggestion has its origin in the valence hypothesis. In cupric chloride,  $\text{CuCl}_2$ , and cupric oxide,  $\text{CuO}$ , copper is evidently bivalent; whereas if the formulas of the cuprous compounds are the simple ones  $\text{CuCl}$ ,  $\text{CuBr}$ , etc., then in them copper is univalent. If, however, cuprous chloride is  $\text{Cu}_2\text{Cl}_2$ , it may be that in it the copper is bivalent. It is only necessary to assume that in the molecule of cuprous chloride two atoms of copper are combined as represented, thus:

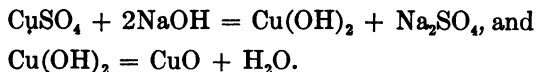


If then each of the copper atoms should combine with a

chlorine atom, the compound would have the formula  $\text{Cu}_2\text{Cl}_2$ . Unfortunately, we have no experimental means of showing whether the molecule of cuprous chloride is  $\text{Cu}_2\text{Cl}_2$  or  $\text{CuCl}$ , so that the above reasoning is purely speculative. It is better, therefore, for the present to keep to the simpler formula. Whatever the explanation may be, it is unquestionably a fact that there are two series of salts of copper, in one of which there is relatively half as much copper as in the other. Mercury, iron, and some other metals present similar phenomena.

**Cuprous oxide**,  $\text{Cu}_2\text{O}$ , is found in nature as *ruby copper*, and is formed when copper is heated in contact with the air. It is a bright-red substance insoluble in water.

**Cupric oxide**,  $\text{CuO}$ , is obtained by heating copper to redness in contact with the air, or by heating the nitrate. It is also formed when caustic soda or potash is added to a boiling-hot solution of a copper salt. If the solution is cold, blue *cupric hydroxide*,  $\text{Cu}(\text{OH})_2$ , is precipitated, but this easily loses water, particularly if the solution is heated. The reactions which take place are:



#### PRECIPITATION OF CUPRIC HYDROXIDE AND FORMATION OF CUPRIC OXIDE.

*Experiment 161.*—Add some caustic soda or potash to a small quantity of a cold solution of copper sulphate in a test-tube. Heat and notice the change from blue to black.

**Copper Sulphate**,  $\text{CuSO}_4 + 5\text{H}_2\text{O}$ .—This salt is manufactured on a large scale and is commonly known by the name "blue vitriol" or "blue stone." [What salt is called "white vitriol"?] It forms large blue crystals, and, when heated, loses water and becomes colorless. The colorless substance becomes blue again in contact with water.

Copper sulphate is used extensively in the preparation of blue and green pigments, in copper plating by electrolysis, in galvanic batteries, for the purpose of preserving wood, and as a remedy against *phylloxera*, an insect that attacks the grape vine and does great damage, and other insects and worms harmful to fruit and vegetables. A solution of copper sulphate is extensively used for spraying fruit trees and young vegetables.

**Copper sulphide**,  $\text{CuS}$ , is a black substance that is formed by passing hydrogen sulphide through a solution of a copper salt, or by adding a soluble sulphide, as potassium sulphide or ammonium sulphide, to such a solution.

#### PRECIPITATION OF COPPER SULPHIDE.

*Experiment 162.*—Treat a dilute solution of copper sulphate with hydrogen sulphide, with ammonium sulphide, with potassium or sodium sulphide.

**Copper arsenite**,  $\text{CuHAsO}_3$ , is formed as a greenish-yellow precipitate when an ammoniacal solution of arsenious acid is added to a solution of cupric sulphate. It is known as *Scheele's green*. A compound of cupric arsenite and cupric acetate, which is made by treating a basic acetate of copper with arsenious acid, is known as *Paris green* or *Schweinfurt green*.



*Paris green* is used to some extent as a pigment, but chiefly as an insecticide for potatoes, cabbage, and other plants.

**Copper-plating.**—The process of copper-plating consists in brief in depositing upon an object a layer of copper by putting it in a bath containing some copper salt and connecting it with the cathode of an electric battery, the anode being a plate or bar of copper. Decomposition of the copper salt takes place, and copper is deposited upon the object. The process is extensively used in the preparation of *electrotype* plates. These are prepared either from wood-cuts or from type by making a mould of plaster of Paris, covering this with graphite, and immersing the mould thus prepared in the copper-plating bath. The plate thus made is an exact reproduction of the wood-cut or type of which the impression was taken.

**Mercury, Hg (At. Wt. 200).**—Mercury occurs native as drops enclosed in rocks, though principally in combination with sulphur as *cinnabar*,  $\text{HgS}$ . It is obtained by roasting *cinnabar*, when vapors of mercury and sulphur dioxide are given off. The mercury is condensed in appropriate vessels. It is a silver-white metal of a high lustre. At ordinary temperatures it is liquid, though it becomes solid at  $-39^{\circ}.5$ . Its specific gravity in terms of water is 13.5995. It does not change in the air at ordinary temperatures. It is insoluble in hydrochloric acid and cold sulphuric acid. [Try each.] It dissolves in hot concentrated sulphuric acid, and is easily soluble in nitric acid. [Try each.] The vapor or mercury is very poisonous.

The total production of mercury in 1905 was 3,110 tons, of which the United States produced 1,036 and Spain 1,020.

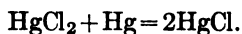
**Uses.**—Mercury is extensively used in the manufacture of thermometers, barometers, etc.; as tin amalgam for mirrors; and in the processes by which gold and silver are obtained from their ores.

**Amalgams.**—With other metals mercury forms alloys (see "Alloys") called *amalgams*. In ordinary galvanic batteries the zinc plates are treated with mercury, and thus covered with a layer of zinc amalgam which protects them from the action of the acids used.

**Compounds of Mercury.**—Among the more common compounds of mercury are the *oxide*,  $\text{HgO}$ ; the two chlorides, *mercurous chloride*,  $\text{HgCl}$ , and *mercuric chloride*,  $\text{HgCl}_2$ ; the two iodides, *mercurous iodide*,  $\text{HgI}$ , and *mercuric iodide*,  $\text{HgI}_2$ ; and the *sulphide*,  $\text{HgS}$ .

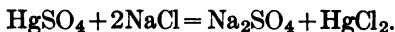
**Mercuric oxide**,  $\text{HgO}$ , is the red substance which was used in one of our first experiments for the purpose of preparing oxygen. It was by heating this substance that oxygen was discovered, and the discovery of oxygen is perhaps the most important event in the history of chemistry. It is formed when mercury is heated for some time near its boiling-point in contact with the air, and is made by heating the nitrate.

**Mercurous chloride**,  $\text{HgCl}$ , is commonly known by the name *calomel*. It is precipitated when a soluble chloride or hydrochloric acid is added to a solution of any mercurous salt. It is manufactured by subliming an intimate mixture of mercuric chloride and mercury:



It is a white substance, insoluble in water, which finds extensive application in medicine.

**Mercuric chloride**,  $\text{HgCl}_2$ , commonly called *corrosive sublimate*, is manufactured on the large scale by subliming an intimate mixture of mercuric sulphate and common salt:



It is a white substance, soluble in water. It is extremely poisonous. It has a very marked influence upon the lower organisms that play so important a part in producing disease and in the decay of organic substances. Wood impregnated with it is partly protected from decay. In surgery it is used for the purpose of preventing contamination of wounds by the hands and instruments of the surgeon.

**Mercuric sulphide**,  $\text{HgS}$ , occurs in nature as cinnabar in the form of red crystals or crystalline masses. When prepared artificially by rubbing mercury and flowers of sulphur together, or by passing hydrogen sulphide through a solution containing a mercury salt, it is a black powder. When sublimed this powder yields red crystals.

**Precipitation of Mercury as Mercurous Chloride.**—It will be noticed that of the two chlorides only mercurous chloride is insoluble in water. If any mercurous salt is present in a solution, mercurous chloride will be thrown down on the addition of a chloride or hydrochloric acid; whereas if the solution contains a mercuric salt the addition of a chloride or hydrochloric acid will not cause precipitation.

**Silver**, Ag (At. Wt. 108).—Silver occurs native; in combination with sulphur; and with sulphur and other metals.

Small quantities of silver sulphide are found in almost all varieties of galenite or lead sulphide. It occurs more rarely as the chloride, bromide, and iodide.

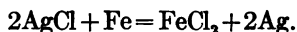
**Metallurgy of Silver.**—Much of the silver in use is obtained from galenite,  $\text{PbS}$ . This mineral is treated in such a way as to cause the separation of the lead (which see), and the silver is separated from sulphur at the same time. But it is dissolved in a large quantity of lead, and the problem that presents itself to the metallurgist is the separation of the small quantity of silver from the large quantity of lead.

**Pattinson's Method.**—This consists in melting the mixture and allowing it to cool until crystals appear. These are almost pure lead. They are dipped out by means of a ladle-sieve, and the liquid left is again allowed to stand, when crystals are again formed, and these are removed in the same way as before. By this means, and by again melting the crystals removed, allowing the liquid to crystallize, and removing the crystals formed, a product rich in silver is finally obtained, but this still contains lead. The lead is then removed by a process known as *cupellation*, which consists in heating the substance on a small hearth of crushed limestone and clay, or of cement, and oxidizing the lead by means of a jet of air which blows the lead oxide toward the front of the hearth, where it is skimmed off. Pattinson's method has been superseded by the

**Zinc Method, or Parkes's Method.**—This consists in treating the molten alloy with zinc, which takes up all the silver. The alloy of zinc and silver thus formed is removed, and the zinc afterward separated by distilling the alloy in a

graphite retort. The product left in the retort still contains about 5 per cent of lead which can be removed by cupellation.

**Amalgamation Process.**—Some ores of silver are treated in another way, known as the *amalgamation process*. The ores are ground and in moist condition mixed with common salt and copper sulphate, when the silver is obtained in the form of the chloride. This is then reduced to silver by means of iron, the reaction taking place as represented in the following equation:



The mixture is next treated with mercury, which forms an amalgam with the silver, while the other metals present do not combine with the mercury. The amalgam can be separated from the rest of the mass without difficulty, and when heated to a sufficiently high temperature the mercury distils over, leaving the silver.

**Refining of Silver.**—Silver is refined by either of two methods:

1. *The Sulphuric Acid Method.*—In this the crude metal is dissolved in sulphuric acid when gold and other valuable metals remain undissolved. From the solution of the sulphate the silver is precipitated by metallic iron. It comes down in finely-divided form. This is pressed into bricks, and melted down.

2. *The Electrolytic Method.*—This is similar to the process used for copper. A solution of silver nitrate is electrolyzed, the cathode being a sheet of pure silver, the anode crude silver which wastes away, regenerating the solution (see Copper). Both of these methods are used in the mints.

Pure silver is technically called "fine silver." (For statistics see Gold.)

**Properties.**—Silver is a white metal with a high lustre. It is not acted upon by air, oxygen, or water. Sulphur acts upon it readily, forming a black coating of silver sulphide. The metal is not dissolved by hydrochloric acid, but is easily dissolved by concentrated sulphuric acid and by dilute nitric acid. The so-called "oxidized silver" is silver coated with the sulphide.

**Alloys of Silver.**—The silver used for coins and most other purposes is an alloy with copper, the pure metal being too soft. The alloy usually contains from  $7\frac{1}{2}$  to 10 per cent of copper. Other metals covered with a layer of silver, deposited by the action of an electric battery, are said to be silver-plated.

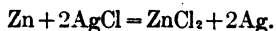
**Compounds of Silver.**—The principal compounds of silver are the *chloride*,  $\text{AgCl}$ ; *bromide*,  $\text{AgBr}$ ; *iodide*,  $\text{AgI}$ ; and *nitrate*,  $\text{AgNO}_3$ .

**Silver nitrate**,  $\text{AgNO}_3$ , is known also by the name "lunar caustic." It is prepared by dissolving silver in dilute nitric acid.

#### PREPARATION OF PURE SILVER NITRATE.

*Experiment 163.*—Dissolve a 10- or a 25-cent piece in dilute nitric acid. [What action takes place?] Dilute the solution to 200–300 cc. with water. [What is the color of the solution? What does this indicate? Does this color prove the presence of copper?] Add a solution of common salt until it ceases to produce a precipitate. [What is the chemical change?] Filter off the white silver chloride and carefully wash with hot water.

Dry the precipitate on the filter by placing the funnel with the filter and precipitate in an air-bath heated to about 100°. Remove the precipitate from the filter and put it into a porcelain crucible. Heat gently with a small flame until the chloride is melted. Cut out a piece of sheet-zinc large enough to cover the bottom of the crucible, and lay it on the silver chloride, after this has become cold. Now add a little water and a few drops of dilute sulphuric acid, and let the whole stand for twenty-four hours. The silver chloride is reduced to silver, and zinc chloride is formed:



This equation does not represent everything that takes place. The sulphuric acid acts upon the zinc, forming nascent hydrogen, and this comes into play to some extent.

Take out the piece of zinc and wash the silver with a little dilute sulphuric acid, and then with water. Heat a small piece of the metal on charcoal in the blowpipe flame until it melts and forms a bead. Dissolve the silver in dilute nitric acid and evaporate to dryness on a water-bath, so that the excess of nitric acid is driven off. Dissolve the residue in water and put the solution either in a bottle of dark glass or in one wrapped in dark paper.

#### PRECIPITATION OF SILVER CHLORIDE, BROMIDE, AND IODIDE.

*Experiment 164.*—To a few cubic centimetres of water in a test-tube add 5 to 10 drops of the solution of silver nitrate just prepared. To this dilute solution add a little of a dilute solution of sodium chloride. The curdy white precipitate is silver chloride. Stand it aside where the light can shine upon it, and notice the change of color which gradually takes place. In the same way make the bromide by adding potassium bromide, and the iodide by adding potassium iodide, to silver nitrate contained in other test-tubes.

**Application of Compounds of Silver in Photography.**—It will be seen from the last experiments that the chloride, bromide, and iodide of silver are insoluble in water and are changed by light. The art of photography is based upon the changes that certain compounds, especially salts of silver, undergo when exposed to the light. Silver iodide is best adapted to most purposes. The salt is so changed by the light that when treated with certain compounds, such as ferrous sulphate, pyrogallie acid, etc., called "developers," a deposit of finely-divided silver is formed upon the plate in those places affected by the light. A plate of glass, a sheet of properly-prepared paper, or a film of gelatin is covered in the dark with a thin layer of a salt of silver. The plate is then exposed in the camera to the action of the light from some object to be photographed. The salt is changed where it is acted upon by the light, while where there is no light it is not acted upon. An image of the object towards which the plate was directed is thus left on the plate. But after the action of the developer is complete there is still upon the plate unchanged silver salt. To remove this the plate is washed with a solution of sodium thiosulphate,  $\text{Na}_2\text{S}_2\text{O}_3$  (hyposulphite), which dissolves the salt. The plate thus obtained is called the "negative."

**Precipitation of Metallic Silver.**—Silver is precipitated from solutions of its salts by zinc, copper, mercury, and some other metals.

#### SILVER-TREE.

*Experiment 165.*—To a solution of silver nitrate containing about 1 gram in 100 cc. water add a few drops of mercury, and let it stand. In a few days the silver will be deposited in the form of delicate crystals. This formation is called the "silver-tree."



**Insoluble Compounds of Silver.**—The oxide, chloride, bromide, iodide, sulphide, carbonate, and phosphate of silver are insoluble in water.

#### INSOLUBLE COMPOUNDS OF SILVER.

*Experiment 166.*—Verify the statement made in the last paragraph. [What takes place when hydrochloric acid is added to a solution of a silver salt? When silver nitrate is added to barium chloride? When ammonium carbonate is added to silver nitrate? When disodium phosphate is added to silver nitrate? In this case, normal silver phosphate,  $\text{Ag}_3\text{PO}_4$ , is formed and some nitric acid is set free.]

**Argentous and Argentic Compounds.**—Silver generally forms compounds that are analogous to the cuprous and mercurous salts, and not those which are analogous to the cupric and mercuric salts. There is, however, an oxide,  $\text{Ag}_2\text{O}$ , and another,  $\text{AgO}$ , corresponding to mercurous and mercuric oxides.

**The Specific Heat of Elements as a Means of Determining their Atomic Weights.**—The question naturally suggests itself, How are the atomic weights determined in the case of elements like silver, copper, etc., which cannot be converted into the form of vapor, and which do not yield compounds that can be converted into vapor? It will be remembered that most of the atomic weights with which we have thus far had to deal, as those of oxygen, chlorine, nitrogen, etc., are determined by a consideration of the specific gravity of the vapors of the compounds of these elements. The relative weights of equal volumes of these

gases or vapors are determined, and then, assuming that these weights express the relative weights of the molecules of the compounds, the smallest weight of the element occurring in any compound is selected as the atomic weight. [Refer back and carefully read the chapter relating to the Atomic Theory and Avogadro's Hypothesis (see pages 87, 174-176; also pages 193, 196, and 200).] But however valuable this method may be, it does not help us in the case of those elements which do not yield compounds capable of conversion into vapor. It has been found that when equal weights of different elements are exposed to exactly the same source of heat, they require different lengths of time to become heated to the same temperature. Given exactly the same heating power, a pound of water must be heated about 32 times as long to raise its temperature 10, 20, or 30 degrees as a pound of mercury must be heated to raise its temperature the same number of degrees; or it takes about 32 times as much heat to raise a pound of water 10, 20, or 30 degrees as it does to raise a pound of mercury the same number of degrees. The quantity of heat required to raise the temperature of a certain weight of a substance one degree as compared with the quantity of heat required to raise the temperature of the same weight of water one degree is called the *specific heat* of the substance. Thus, from what was said above, the specific heat of mercury is nearly  $\frac{1}{32}$ , or, in decimals, 0.0319. In a similar way it can be shown that the specific heat of gold is 0.0324; of zinc, 0.0955; of silver, 0.057; of copper, 0.0952. But these figures bear a remarkable relation to the atomic weights found by means of analysis. Thus, taking the above elements, we have:

	Specific Heat.	At. Weight.
Mercury.....	0.0319	200
Gold.....	0.0324	197
Zinc.....	0.0955	65
Silver.....	0.057	108
Copper.....	0.0952	63.5

Calculation will show that the specific heat of these elements is approximately inversely proportional to their combining weights. Thus,

$$\begin{array}{ccccccc}
 0.0319 & : & 0.057 & :: & 108 & : & 200. \\
 \text{Sp. Ht. of Hg.} & & \text{Sp. Ht. of Ag.} & & \text{At. Wt. of Ag.} & & \text{At. Wt. of Hg.}
 \end{array}$$

And the same is true in most other cases. Or the relation may be stated in another way, *viz.*: The product of the specific heat of any element multiplied by its atomic weight is the same in all cases. The product is about 6.25. This, which is known as the law of Dulong and Petit, may be stated thus:

*The atomic weight of an element multiplied by its specific heat is a constant which has a value of about 6.25.*

There are some exceptions to the law, but these cannot be discussed at this time. Despite its imperfections it has furnished a valuable means of determining atomic weights. If A represents the atomic weight, and S the specific heat, then, according to the law of Dulong and Petit,  $A \times S = 6.25$  nearly, and  $A = \frac{6.25}{S}$ . To determine the atomic weight of

an element by this method, then, it is only necessary to determine the specific heat of the element. Substituting for S the figure found, the value of A can be easily calculated. By careful analysis of compounds of the element the figure can be determined more accurately.

## CHAPTER XXIV.

### THE ALUMINIUM GROUP: ALUMINIUM, GALLIUM, INDIUM, THALLIUM, SCANDIUM, YTTRIUM, LANTHANUM, AND YTTERBIUM.

**General.**—The only element of this group that need be treated of here is aluminium. This is an extremely important element that is found very widely distributed in nature.

**Aluminium, Al** (At. Wt. 27).—Among the many important and widely-distributed minerals that contain aluminium are feldspar, granite, mica, and cryolite.

Feldspar is a silicate of aluminium and potassium of the formula  $\text{AlKSi}_3\text{O}_8$ . Mica is a general name applied to a large number of minerals which are silicates of aluminium and some other metal, as potassium, lithium, magnesium, etc. The simplest form of mica is that represented by the formula  $\text{KAlSiO}_4$ , according to which the mineral is a salt of orthosilicic acid,  $\text{Si}(\text{OH})_4$ . Cryolite is a double fluoride of aluminium and sodium, or the sodium salt of fluo-aluminic acid,  $\text{Na}_3\text{AlF}_6$ . Bauxite is a hydroxide of aluminium in combination with a hydroxide of iron. Aluminium occurs in the products of decomposition of minerals, as well as in the above forms. One of the most important of these is clay, which is found in all conditions of purity, from white

kaolin to ordinary dark-colored clay. Kaolin is the aluminium salt of orthosilicic acid of the formula  $\text{Al}_4(\text{SiO}_4)_3 + 4\text{H}_2\text{O}$ . Aluminium silicate is found in all soils, but is not taken up by plants, and does not find entrance into the animal body. The name aluminium has its origin in the fact that alum was known at an early date, and the metal was afterwards shown to be contained in this.

**Preparation.**—The preparation of aluminium on the large scale is an important problem. The element has properties which would appear to adapt it to most uses to which iron is put, and for many purposes it has advantages over iron. Further, nature supplies us with unlimited quantities of the compounds of aluminium, which are distributed everywhere over the earth. While, however, iron, lead, tin, copper, and other metals can be isolated from their natural compounds without serious difficulty, aluminium, which is more abundant than any of them, and in some respects more valuable than any of them, is locked in its compounds so firmly that it cannot be as readily obtained.

It is best prepared by the electrolysis of aluminium oxide,  $\text{Al}_2\text{O}_3$ . This is melted in a bath of fused cryolite contained in iron pots which have thick carbon linings. The pot itself forms the cathode, while a number of large graphite rods suspended in the bath form the anode. Bauxite (see page 438) is the principal source of the aluminium oxide or alumina.

In the year 1906, 7,500 tons of aluminium was produced in the United States and in 1905, 5,674. In 1888 the price was \$4 a pound; in 1893 it ranged from 65 to 75 cents; in 1907 it was about 50 cents. The lightness

of aluminium must be considered in comparing it with other metals; bulk for bulk, aluminium is cheaper than copper and nearly as cheap as zinc.

**Properties.**—The color of aluminium is like that of tin, and it has a high lustre. It is very strong, and yet malleable. It is lighter than most metals in common use, its specific gravity being 2.5 to 2.7 according to the condition, while that of iron is 7.8, that of silver 10.57, that of tin 7.3, and that of lead 11.37. It does not change in dry or in moist air; and in the compact form it does not act upon water even at elevated temperatures. It melts at about 700°, which is higher than the melting-point of zinc, and lower than that of silver. Hydrochloric acid dissolves it with ease, forming aluminium chloride. At ordinary temperatures nitric and sulphuric acids do not act upon it; at higher temperatures, however, action takes place, and the corresponding salts are formed. It dissolves in solutions of the caustic alkalies, forming the so-called aluminates. It reduces many oxides when heated with them to a high temperature; and it is used in the preparation of boron and silicon.

**Applications.**—The metal is used to a considerable extent in the preparation of ornaments and of useful articles in which lightness is of importance, as in telescopes and opera-glasses. An alloy with a small percentage of silver is used for the beams of chemical balances. Aluminium bronze, which is an alloy with copper, is also used quite extensively. (See under Copper, page 423.) Magnalium is an interesting alloy of aluminium with magnesium.

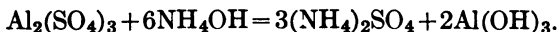
High temperatures (about 3000° C.) are attained by burning cartridges containing a mixture of aluminium and ferric oxide. Practical use is made of this process in welding. It is known as the Goldschmidt process.

**Compounds of Aluminium.**—Among the more important compounds of aluminium are the *oxide*,  $\text{Al}_2\text{O}_3$ ; the *hydroxide*,  $\text{Al}(\text{OH})_3$ ; the *sulphate*,  $\text{Al}_2(\text{SO}_4)_3$ ; the *alums*; the *silicates*; and the *chloride*,  $\text{AlCl}_3$ .

**Aluminium Oxide**,  $\text{Al}_2\text{O}_3$ .—This compound, also called *alumina*, occurs in nature in the form of ruby, sapphire, and corundum. It is very hard, and as *emery* is used for polishing. It is made artificially by heating the hydroxide,  $\text{Al}(\text{OH})_3$ :



**Aluminium Hydroxide**,  $\text{Al}(\text{OH})_3$ .—This compound is found in nature in crystallized form as hydrargillite. It is precipitated when ammonia is added to a solution of aluminium sulphate:



It forms a gelatinous mass which it is difficult to filter. [Precipitate some from a solution of ordinary alum.] The hydroxide is soluble in acids and in alkalies. In the former case salts are formed in which the hydroxide plays the part of a base; in the latter it acts like an acid. The salts formed with the alkalies are called *aluminates*. In aluminium salts one atom of the metal replaces three atoms of hydrogen;

thus, aluminium nitrate is  $\text{Al}(\text{NO}_3)_3$ ; the sulphate,  $\text{Al}_2(\text{SO}_4)_3$ , etc. In the aluminates the three hydrogen atoms of the hydroxide are replaced by metal; thus, potassium aluminate is  $\text{Al}(\text{OK})_3$ , and sodium aluminate  $\text{Al}(\text{ONa})_3$ .

#### PRECIPITATION AND SOLUTION OF ALUMINIUM HYDROXIDE.

*Experiment 167.*—Precipitate some aluminium hydroxide from a dilute solution of alum, by means of caustic potash, and continue to add the latter slowly, when the precipitate will dissolve. Do the same with caustic soda.

Aluminium hydroxide,  $\text{Al}(\text{OH})_3$ , loses water when heated, and a compound of the formula  $\text{AlO}_2\text{H}$  is formed:



This compound is found in nature as the mineral diaspore. It has acid properties and forms extremely stable salts, several of which are found in nature. Spinel is magnesium aluminate,  $(\text{AlO}_2)_2\text{Mg}$ . The formation of the hydroxides  $\text{Al}(\text{OH})_3$  and  $\text{AlO}_2\text{H}$ , and of salts derived from each, indicates some analogy between aluminium and boron. On the other hand, the power to replace the hydrogen of acids is not possessed by boron to any great extent. [Refer back to Boron, page 322. Read again what is said about it, and compare it with aluminium.]

**Aluminium Sulphate,**  $\text{Al}_2(\text{SO}_4)_3 + 18\text{H}_2\text{O}$ . This salt is usually prepared from bauxite (see page 438) or from pure kaolin (see page 444). In pure form it finds extensive application under the name "concentrated alum." It is used in dyeing, in the preparation of size for paper, for precipitating sewage or coloring-matter from water. Alum was



formerly used for these purposes, but this "concentrated alum" has taken its place.

**Alums.**—With the sulphates of the alkali metals aluminium sulphate forms complex compounds which crystallize beautifully. Potassium alum is the best known of these. It may be regarded as derived from 2 molecules of sulphuric acid by the replacement of 3 atoms of hydrogen by 1 atom of aluminium, and the fourth by 1 atom of potassium; thus,  $\text{AlK}(\text{SO}_4)_2$ . The crystals always contain 12 molecules of water, the complete formula being  $\text{AlK}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ . Similarly, sodium alum is  $\text{AlNa}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ , and ammonium alum  $\text{AlNH}_4(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ .

#### ALUM.

*Experiment 168.*—Determine whether the alum in the laboratory contains potassium or ammonium. Crystallize some. What forms do the crystals possess?

**Applications.**—Alum is used very extensively in the preparation of pigments, as a mordant,\* in the sizing of paper, for clarifying water, etc.

\* In dyeing with dyes like indigo or Prussian blue, an insoluble colored precipitate is formed in the fibre of the substance dyed. Hence such dyes form fast colors with any fabric. The majority of the dyes used are soluble in water.

*Substantive dyes* are those which can be removed from their solution by contact with a fabric, combining with the fibre to form colors more or less fast according to the nature of the fibre.

*Adjective dyes* are those which do not combine directly with the fibre but require the use of a mordant. Salts of aluminium and of tin are common mordants. On treating the fabric with the mordant the latter combines with the fibre of the fabrics. On treating the mordanted fabric with the dye, the dye forms a fast color (or insoluble chemical compound) with the mordant.

**Aluminium Silicate.**—The silicate of aluminium occurs in nature in enormous quantities. The most important of the minerals containing it are the feldspars, of which ordinary feldspar,  $\text{KAlSi}_3\text{O}_8$ , is the most abundant. The feldspars, further, enter into the composition of granite together with quartz and mica, and mica itself is a double silicate of aluminium.

**Natural Decomposition of Feldspar.**—Under the influence of moisture, the carbon dioxide of the air, and changes in temperature, the feldspars are undergoing slow decomposition, the products being mainly potassium or sodium silicate and aluminium silicate. The salts of the alkali metals, principally the potassium salt, being soluble, are carried away, and find their way into the soil. The silicate of aluminium is not soluble, but it easily forms an emulsion with water, and is therefore carried down the sides of the hills and mountains upon which it is formed into the valleys, and much of it finds its way into streams. Sometimes this carrying away is prevented, and then beds of comparatively pure clay, known as kaolin, are formed. The clay found in the valleys is always more or less impure and colored.

**Kaolin.**—This is the purest form of aluminium silicate found in nature. It always contains water. Its composition varies, some specimens on analysis giving results which lead to the formula  $\text{Al}_4(\text{SiO}_4)_3 + 4\text{H}_2\text{O}$ , according to which the substance is the salt of normal silicic acid,  $\text{Si}(\text{OH})_4$ . Other specimens have the composition  $\text{HAlSiO}_4 + \text{H}_2\text{O}$ . When heated alone kaolin does not melt; but if feldspar is added to it, the whole melts and forms a translucent mass known

as *porcelain*. Other substances besides feldspar may be used for this purpose.

**Clay.**—Ordinary clay, as has been stated, is a name given to the impure varieties of aluminium silicate which have been carried down from the place of formation. Among the substances besides aluminium silicate found in clays are calcium carbonate, magnesium carbonate, sand, and hydroxides of iron. The color is largely determined by the amount of the hydroxides of iron present. The better varieties are used in the manufacture of the so-called “stone-ware,” gas-retorts, and fire-bricks. The colored varieties are used in making ordinary earthenware and bricks. *Marl* is clay mixed with considerable quantities of calcium carbonate.

**Ultramarine.**—The substance occurring in nature and known as *lapis lazuli* consists of a silicate of sodium and aluminium together with a sulphur compound, probably a polysulphide of sodium. The coloring-matter, known as ultramarine, obtained by powdering it was formerly very expensive, but it is now made artificially by the ton, and the color of the artificially prepared substance is even more beautiful than that of the natural. The artificial preparation is effected by melting together kaolin, anhydrous sodium carbonate, and sulphur, or clay, calcined sodium sulphate, and charcoal. By varying the conditions of preparation, products of different colors are obtained. Besides the deep-blue ultramarine, there are now manufactured ultramarines of different shades of blue, and a green variety.

Ultramarine is manufactured in very large quantity—according to a recent report, to the extent of nearly 9000

tons a year. It is the most extensively used blue coloring-matter.

**Porcelain.**—It was stated above that when kaolin is heated alone it does not melt, but that if feldspar is added to it, or if that found in nature contains feldspar, as is frequently the case, it either fuses together forming a compact mass, or melts and forms a translucent mass. Further, when kaolin or any other variety of clay is mixed with water, a plastic substance results, which can be kneaded and worked into any desired form. These facts form the basis of the manufacture of earthenware, porcelain, etc. The ease with which the mass melts depends upon the quantity of feldspar or other flux added to it. If but little is added, it melts with difficulty; if much is added it melts easily.

In the manufacture of the finest kinds of porcelain kaolin is used. This is generally mixed with a little feldspar or chalk, gypsum, or some other flux, and sand is also added. All these substances must be very finely ground. The mixture is then worked into the desired forms and carefully dried. After the objects are dried they are burned, first at a red heat at which the mass becomes solid, afterwards at a white heat for the purpose of forming a glaze upon the surface. The product after the first burning is that which is familiar as porous earthenware; that formed in the second burning is the porcelain with glaze as it is commonly used.

In order to form the glaze upon the porcelain the porous earthenware first formed is drawn through a vessel containing proper materials in finely powdered condition and suspended in water. The materials used are generally

the same as those used for the porcelain itself, but they are mixed in different proportions, with less kaolin and more sand and feldspar, so as to be more easily fusible. After this treatment the objects are again heated to a high temperature.

**Earthenware.**—The ordinary varieties of earthenware are made from clays which are much less pure than kaolin. Ordinary colored clay is used. The objects are formed, and then subjected in general to the same kind of treatment as porcelain. They are glazed in different ways. One method consists in bringing the glazing material on the earthenware before it is burned; another method consists in putting the objects in the furnace without a glaze, and towards the end of the firing process sodium chloride is thrown into the furnace, and is thus brought in contact with the ware in the form of vapor. A chemical change takes place, resulting in the formation of a silicate of aluminium and sodium upon the surface. This melts and forms a glaze.

Bricks are the most common variety of unglazed earthenware. Owing to the presence of other substances besides aluminium silicate, as, for example, calcium carbonate, the material is comparatively easily fusible. The color of red bricks is largely due to the presence of oxides of iron.

**Action of Soluble Carbonates and Soluble Sulphides on Solutions of Aluminium Salts.**—With weak acids aluminium forms no salts. There is, for example, no carbonate. The sulphide is so unstable that it is decomposed into the hydroxide and hydrogen sulphide when exposed to moist

air. When a soluble hydroxide is added to a solution of a salt of aluminium, the insoluble hydroxide is at first precipitated; but, as this has weak acid properties as well as weak basic properties, it dissolves in an excess of either caustic soda or caustic potash. Owing to the fact that the basic properties of the hydroxide are so weak, sodium carbonate and other soluble carbonates precipitate, not the carbonate, but the hydroxide of aluminium.

#### PRECIPITATION OF ALUMINIUM HYDROXIDE BY SOLUBLE CARBONATES.

*Experiment 169.*—Add a dilute solution of sodium carbonate to a dilute solution of alum. The precipitate is the hydroxide,

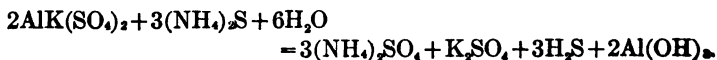


Filter off and, after washing carefully, see whether the precipitate is the carbonate. Try the same experiment with ammonium and potassium carbonates.

When an aluminium salt in solution is treated with ammonium sulphide, the hydroxide is precipitated. Even if the sulphide were formed it would be decomposed into the hydroxide and hydrogen sulphide by water.

#### PRECIPITATION OF ALUMINIUM HYDROXIDE BY AMMONIUM SULPHIDE.

*Experiment 170.*—Add ammonium sulphide to a solution of alum. The precipitate is aluminium hydroxide,



**Rare Elements of the Aluminium Group.**—The other members of the aluminium group need not be taken up here. The existence and properties of two of them, gallium and scandium, were predicted by the aid of the periodic law, as has been pointed out (see page 265).

## CHAPTER XXV.

### THE LEAD GROUP: LEAD, TIN, AND GERMANIUM.

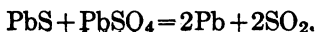
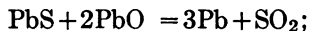
**General.**—The only two members of this group that need be studied here are lead and tin. There are some points of resemblance between them, but there are also marked differences.

**Lead, Pb (At. Wt. 207).**—Lead occurs in combination in several forms in nature; for example, as the sulphate, carbonate, chromate, and sulphide. The sulphide PbS, known as galenite or galena, is the most important source of lead.

**Metallurgy.**—The extraction of the metal from the sulphide is accomplished in one of two ways:

(1) By heating the sulphide with iron, when the latter combines with the sulphur, forming iron sulphide, while the lead is set free.

(2) By roasting the sulphide until it is partly converted into lead oxide and lead sulphate, and then heating the mixture without access of air, when the following two reactions take place:





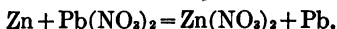
The lead is thus set free, and the sulphur is driven off as sulphur dioxide.

Some lead is now made by the electrolysis of galena. In this process it is obtained in the form of a spongy mass. The production of lead has doubled within the last fifteen years. In 1906 it was 921,679 tons, of which the United States produced 341,379.

**Properties.**—Lead is a bluish-gray metal with a high lustre. It is very soft and not very strong. It melts at about 325°. All lead compounds are poisonous. Nitric acid dissolves it, but hydrochloric and dilute sulphuric acids do not. It is precipitated in metallic form from a solution of one of its salts by metallic zinc. The formation is sometimes called the “lead-tree” or “Arbor Saturni.”

#### DECOMPOSITION OF A LEAD SALT BY ZINC.

*Experiment 171.*—Dissolve 5 grams lead nitrate \* in a litre of water and add 2–3 drops dilute nitric acid. Put the solution in a bottle. By means of a thread suspend a piece, about an inch or an inch and a half square, of clean sheet zinc in the solution and let it stand. The lead will be deposited slowly in crystalline form. At the same time the zinc will pass into solution. The zinc replaces the lead:



After the tree is formed, filter off some of the solution and see whether zinc is contained in it or not. There will probably be some lead left, so that in order to detect the zinc the lead will have to be removed first. This may be done by adding sulphuric acid and alcohol. The sulphate of lead is thus formed. As this

\* Instead of lead nitrate, the acetate (sugar of lead) may be used.

is somewhat soluble in water and insoluble in alcohol, the latter is added. Filter off the lead sulphate, and to the filtrate add just enough ammonia to neutralize the sulphuric acid, and then ammonium sulphide. White zinc sulphide is precipitated.

If all the lead is not precipitated by the sulphuric acid, the precipitate caused by ammonium sulphide will not be white, but more or less inclined towards black, according to the quantity of lead sulphide present. All the lead may be precipitated in the first instance by first adding some hydrochloric acid [What effect will this have on the solution of the lead salt? Which chlorides are insoluble?] and then passing hydrogen sulphide through the solution. Filter off, wash, and add ammonia and ammonium sulphide to the filtrate.

**Uses.**—Lead is extensively used for a variety of purposes, as, for example, for sulphuric-acid chambers, for evaporating-pans for alum and sulphuric acid, for shot, for water-pipes, and for making a number of valuable alloys. The use of lead water-pipes is a matter of much importance from a sanitary point of view. Ordinary drinking-water acts only very slightly upon lead, and not enough is dissolved to be dangerous. Nevertheless, circumstances may at any time arise that will increase the solvent power of the water and serious results may follow. Air and water act together upon lead more readily than when the air is excluded. In moist air lead tarnishes. *Babbitt's metal*, which is used for machine bearings, contains copper, antimony, tin, and lead. Much lead is now used in making storage batteries.

**Compounds of Lead and Oxygen.**—Lead forms three distinct compounds with oxygen, viz.: *lead suboxide*,  $Pb_2O$ ; *lead oxide*,  $PbO$ ; and *lead peroxide*,  $PbO_2$ . *Red lead*, or

*minium*, has approximately the composition  $Pb_3O_4$ , and is a mixture or a compound of the oxide and peroxide. It is used as a pigment, and sometimes in place of litharge when an oxide of lead is needed, as in the manufacture of glass, as a flux in the manufacture of porcelain, etc.

**Lead oxide**,  $PbO$ , is known by the name of *litharge*. It is formed by the oxidation of molten lead in contact with the air. When litharge is heated in the air to  $400^\circ$  it takes up oxygen and is converted into *minium*, or *red lead*,  $Pb_3O_4$  ( $= 2PbO + PbO_2$ ). When heated to a high temperature this gives up oxygen and is again converted into yellow lead oxide. Treated with nitric acid, a part is dissolved forming lead nitrate, while lead peroxide, a brown powder, remains behind.

#### FORMATION OF LEAD PEROXIDE FROM MINIMUM.

*Experiment 172.*—(tt) Treat a little minium with ordinary dilute nitric acid, and note the change in color. [Does lead pass into solution? How do you know?]

**Lead peroxide**,  $PbO_2$ , conducts itself somewhat like manganese dioxide. When treated with hydrochloric acid chlorine is evolved:



#### ACTION OF HYDROCHLORIC ACID ON LEAD PEROXIDE.

*Experiment 173.*—Treat a little lead peroxide with concentrated hydrochloric acid in a test-tube. [In what form is the lead after the experiment? Is the product soluble or insoluble in water?]

When heated with sulphuric acid, lead peroxide gives off oxygen and yields lead sulphate.

## ACTION OF SULPHURIC ACID ON LEAD PEROXIDE.

*Experiment 174.*—(tt) Heat some lead peroxide with concentrated sulphuric acid. [Is oxygen given off? What is left behind? Is it soluble or insoluble?]

**Storage Battery.**—An efficient galvanic battery can be made by putting two lead plates in dilute sulphuric acid, one of the plates being covered with a layer of lead peroxide. The sulphuric acid acts upon the lead, converting it into lead sulphate, which forms a solid layer upon the plate. On the other hand, the acid acts upon the lead peroxide, reducing the lead to the bivalent condition and forming with it lead sulphate. As long as the chemical action can take place, that is to say, as long as there is lead peroxide present, the battery continues to act. When it ceases to act it can be restored to the active condition by passing an electric current through it in the opposite direction. Under these conditions the lead sulphate on one plate is reduced to metallic lead, and that on the other is oxidized to lead peroxide. These facts are taken advantage of in the preparation of the well-known storage batteries.

**Salts of Lead.**—Among the more important salts of lead are the *sulphate*,  $\text{PbSO}_4$ ; the *nitrate*,  $\text{Pb}(\text{NO}_3)_2$ ; the *carbonate*,  $\text{PbCO}_3$ ; the *acetate*,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ ; the *chromate*,  $\text{PbCrO}_4$ ; and the *sulphide*,  $\text{PbS}$ . The acetate and nitrate are soluble in water; the others are not.

**Lead acetate**,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , commonly called “sugar of lead,” is the lead salt of acetic acid,  $\text{C}_2\text{H}_4\text{O}_2$ , which is the acid contained in vinegar. The acetate is formed by dissolving litharge in acetic acid.

**Insoluble Salts of Lead.**—The sulphate, chromate, and chloride have already been referred to. They are formed by adding a soluble sulphate, chromate, and chloride to a solution of a lead salt. The chromate is the well-known *chrome yellow*. Lead chloride is soluble in hot water, but only slightly soluble in cold water. It crystallizes from its solution in hot water.

#### FORMATION AND CRYSTALLIZATION OF LEAD CHLORIDE.

*Experiment 175.*—To a dilute solution of lead nitrate or acetate add some hydrochloric acid. Heat and thus dissolve the precipitate and stand it aside. On cooling, the lead chloride will crystallize out. It is not soluble in ammonia. [Does it differ from silver chloride in this respect?]

**Lead carbonate**,  $\text{PbCO}_3$ , occurs in nature as cerussite, and is precipitated by adding lead nitrate to a solution of ammonium carbonate; but when a solution of a lead salt is treated with a normal carbonate of sodium or potassium, a basic carbonate is precipitated. When, for example, an excess of sodium carbonate is added to a solution of lead nitrate, the precipitate has the composition  $3\text{PbO} \cdot 2\text{CO}_2 + \text{H}_2\text{O}$ . The salts usually obtained are more complicated than this. Basic lead carbonate is prepared and used extensively under the name of *white lead*, as a pigment. An objection to white-lead paint is that it turns dark when exposed to hydrogen sulphide. It also turns yellow in consequence of the action of some substance contained in the oil with which the lead carbonate is mixed.

**Lead sulphide**,  $\text{PbS}$ , is the important mineral galenite or galena to which reference has been made. The compound is

precipitated by passing hydrogen sulphide through a solution of a lead salt, or by adding a soluble sulphide to such a solution.

[How can you distinguish between a lead and a barium salt without using hydrogen sulphide? Between lead and silver without using hydrogen sulphide or hydrochloric acid? By hydrochloric acid alone?]

**Tin, Sn (At. Wt. 119).**—Tin occurs in nature mostly as tin-stone, or cassiterite, which is the oxide  $\text{SnO}_2$ .

**Metallurgy.**—The ores are roasted for the purpose of getting rid of the sulphur and arsenic, and the oxide is then heated with coal in a furnace. After the reduction is complete the tin is drawn off and cast in bars. This tin is impure, and when again slowly melted, that which first melts is purer. By letting it run off as soon as it melts, the comparatively difficultly fusible alloy remains behind. The commercial variety known as *Banca tin* is the purest. This is made at Banca in the East Indies. Block tin, made in England, is also comparatively pure.

**Properties.**—Tin is a white metal, which in general appearance resembles silver. It is soft and malleable, and can be hammered out into very thin sheets, forming thus the well-known tin-foil. At  $200^\circ$  it is brittle. It melts at  $228^\circ$ . It remains unchanged in the air at ordinary temperatures. It dissolves in hydrochloric acid, forming stannous chloride,  $\text{SnCl}_2$ ; in sulphuric acid, forming stannous sulphate,  $\text{SnSO}_4$ , sulphur dioxide being evolved at the same time. [Explain this.] Ordinary concentrated nitric acid oxidizes it, the product being a compound of

tin, oxygen, and hydrogen, known as *metastannic acid*, which is a white powder insoluble in nitric acid and in water.

**Uses.**—Tin is used in making alloys, of which bronze, soft solder, and britannia metal are the most important. It is used most extensively for protecting other metals, as in the tinware vessels in such common use, which are made of sheet iron covered with a layer of tin.

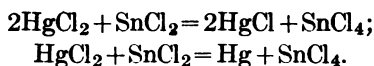
**Alloys.**—Bronze has already been referred to under Copper (page 423). *Soft solder* is made of equal parts of tin and lead, or of two parts of tin and one of lead. *Britannia metal* is composed of nine parts of tin and one of antimony. *Tin amalgam* is made by bringing tin and mercury together, and was formerly used in the silvering of mirrors.

**Stannous and Stannic Compounds.**—Tin forms two classes of compounds, the *stannous* and *stannic* compounds. These do not bear to each other the same relation that cuprous and cupric compounds do. [What is this?] In stannous compounds the tin appears to be bivalent, as indicated by the formulas  $\text{SnCl}_2$ ,  $\text{SnO}$ ,  $\text{SnS}$ , which respectively represent stannous chloride, oxide, and sulphide. In stannic compounds, on the other hand, the tin appears to be quadrivalent, as indicated by the formulas  $\text{SnCl}_4$ ,  $\text{SnO}_2$ , and  $\text{SnS}_2$ , which respectively represent stannic chloride, oxide, and sulphide.

In general, stannous compounds are readily converted into stannic compounds.

**Stannous chloride**,  $\text{SnCl}_2$ , is formed by dissolving tin in hydrochloric acid. If a solution of stannous chloride is added to a solution of mercuric chloride (corrosive sub-

limate), the latter is reduced to mercurous chloride, and this, being insoluble in water, appears as a precipitate. When stannous chloride and mercuric chloride are heated together in solution, metallic mercury is formed:



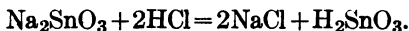
#### REDUCTION OF MERCURIC CHLORIDE BY STANNOUS CHLORIDE.

*Experiment 176.*—Dissolve a few grams of tin in warm ordinary concentrated hydrochloric acid. Add a little of this solution to a solution of mercuric chloride. A white precipitate of mercurous chloride will be formed. Heat the two solutions together, and notice the formation of metallic mercury, which appears as a gray powder.

**Stannic oxide**,  $\text{SnO}_2$ , occurs in nature as tin-stone. It is obtained by burning tin in the air. When melted together with caustic soda it dissolves as sodium stannate. This action suggests that which takes place when silicon dioxide is melted with an alkali and a silicate is formed, and when carbon dioxide and an alkali are brought together. The formulas of the products in these cases are similar, *viz.*,  $\text{Na}_2\text{SnO}_3$ ,  $\text{Na}_2\text{SiO}_3$ , and  $\text{Na}_2\text{CO}_3$ .

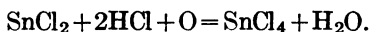
**Stannic Hydroxide**,  $\text{Sn}(\text{OH})_4$ , and **Stannic Acid**,  $\text{H}_2\text{SnO}_3$ .—Stannic hydroxide,  $\text{Sn}(\text{OH})_4$ , is perhaps formed when a solution of stannic chloride in water is boiled. The precipitate obtained has, however, the composition  $\text{H}_2\text{SnO}_3$ , and this is known as stannic acid. Stannic acid is precipitated also by treating a solution of a stannate with just enough of an acid to effect decomposition. The decomposition with hydrochloric acid takes place as represented in the equation





**Metastannic Acid.**—When tin is treated with concentrated nitric acid it is converted into a white powder which is insoluble in water and in acids. Stannic acid is insoluble in water, but is easily soluble in hydrochloric, nitric, and sulphuric acids. The two acids cannot, therefore, be identical though they appear to have the same composition. The product formed by oxidizing tin with nitric acid is called metastannic acid.

**Stannic chloride**,  $\text{SnCl}_4$ , is made by heating tin in chlorine. It is a heavy liquid that boils at  $120^\circ$  without decomposition. It fumes in the air very strongly. It has a marked affinity for water, and is used as a dehydrating agent in a number of reactions. It has long been known by the name *spiritus fumans Libavii*. In solution it is obtained by dissolving tin in *aqua regia*. In this case the stannous chloride formed by the action of the hydrochloric acid on the tin is oxidized by the nitric acid:



**Stannic sulphide**,  $\text{SnS}_2$ , is a yellow substance resembling arsenic sulphide. It is formed by passing hydrogen sulphide through a dilute solution of stannic chloride. It is soluble in ammonium sulphide.

#### PRECIPITATION OF TIN AS SULPHIDE.

*Experiment 177.*—Dissolve a little tin in a little hydrochloric acid. Boil the solution, add a few drops of nitric acid, and continue to boil. Dilute the solution, heat it, and pass hydrogen

sulphide through it. Filter, wash the precipitate, and treat on the filter with ammonium sulphide. [Does the precipitate dissolve? Dilute the filtrate, and add an acid to it. What takes place?]

**How to Distinguish Tin from Other Metals.**—A peculiarity of tin which distinguishes it from most other metals is its conduct towards nitric acid. As already stated, instead of dissolving in the acid, it is converted into a white, insoluble compound—metastannic acid. Antimony is also converted into a white oxide by nitric acid, but antimony does not dissolve in hydrochloric acid, while tin does.

**ACTION OF NITRIC ACID ON TIN AND ON ANTIMONY. ACTION OF HYDROCHLORIC ACID ON THE SAME ELEMENTS.**

*Experiment 178.*—Treat a little tin with strong nitric acid, and notice the formation of the white metastannic acid. [Is it soluble in water?] Treat a little antimony in the same way. Now treat each element separately with hydrochloric acid.

**ANALYSIS OF SOLDER.**

*Experiment 179.*—Examine a small piece of solder, and determine whether it contains lead and tin.—Treat with *aqua regia*; dilute with water. [Will all the lead pass into solution under these circumstances?] Heat and pass hydrogen sulphide through the much-diluted solution. Filter off the precipitate; wash with hot water; treat with yellow ammonium sulphide; filter; add an acid to the filtrate. [Explain what takes place in each step.] The formation of a yellow precipitate, which is soluble in ammonium sulphide, is not conclusive evidence that tin is present, for arsenic sulphide has similar properties. In order to distinguish between them advantage may be taken of the fact that arsenic sulphide is soluble in a solution of ammonium carbonate, while stannic sulphide is not. Treat some of the precipitate, which has been

thoroughly washed, with a solution of ammonium carbonate; filter; add an acid, when, if any arsenic sulphide is in solution, it will be precipitated. Filter if a precipitate is formed. Test for lead by means of sulphuric acid.

#### BRONZE.

*Experiment 180.*—Dissolve a small amount of bronze, which is an alloy of tin and copper, in hot *aqua regia* and, after evaporating off most of the acid, dilute with ten times its volume of hot water. Saturate the solution with hydrogen sulphide to precipitate the sulphides of the metals and filter and wash. When this precipitate is treated on the filter-paper with ammonium sulphide the tin sulphide passes through in solution, while the copper sulphide remains on the filter. The sulphide of tin can be precipitated from the solution by the action of an acid, and can be tested for arsenic by the method given in the previous experiment. Dissolve the black copper sulphide in warm dilute nitric acid and add small pieces of solid sodium hydroxide until the excess of acid is neutralized and the copper is precipitated as blue copper hydroxide. If the solution is hot, the hydroxide is changed to the black oxide, which can be filtered and reduced to metallic copper, if it is mixed with sodium carbonate and heated in the reducing flame of the blowpipe.

## CHAPTER XXVI.

### THE IRON GROUP: IRON, COBALT, NICKEL.

**Iron, Fe** (At. Wt. 56).—At the present time it is undoubtedly true that iron is the most important metal for man. It is not improbable, however, that in the future aluminium may take its place for some purposes, though there is no immediate prospect of this interference with the iron industry.

**Occurrence.**—Iron occurs in the form of the oxides,  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ ; as the carbonate,  $\text{FeCO}_3$ ; in combination with sulphur as iron pyrites, pyrite,  $\text{FeS}_2$ ; and as silicates and hydrated oxides, or hydroxides. The compounds principally used in making iron are magnetite,  $\text{Fe}_3\text{O}_4$ ; hæmatite,  $\text{Fe}_2\text{O}_3$ ; brown iron ore,  $\text{Fe}_4\text{O}_3(\text{OH})_6$ ; and spathic iron, or siderite,  $\text{FeCO}_3$ . Native iron occurs in meteorites and is also sometimes disseminated in fine particles in basaltic rock.

**Metallurgy.**—After the ores are broken up, they are first roasted (see page 333), in order to drive off water from the hydroxides; to decompose carbonates; to oxidize sulphides; and, as far as possible, to convert the oxides into ferric oxide,  $\text{Fe}_2\text{O}_3$ , which is the most easily reducible of the oxides of iron. After the ores are prepared in this way

they are reduced by heating them with carbon and fluxes in the blast-furnace, when the iron collects in the molten

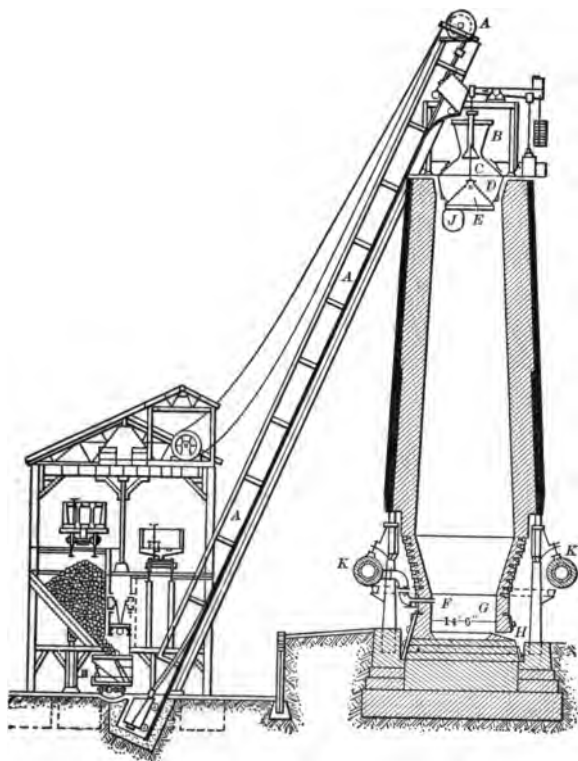


FIG. 53.

condition under the so-called slag at the bottom of the furnace.

Blast-furnaces differ somewhat in construction, but the essential parts are represented in Fig. 53. The inner walls of the furnace are made of fire-bricks, and these are surrounded by ordinary bricks or stonework. The fur-

naces vary in height from 25 to 80 or 90 feet. Those having a height of 90 feet seem to have the greatest efficiency. The ore with coke and limestone is carried to the top of the furnace by a hoist *A.A.* It is there brought into the hopper *B.* By lowering the bell *C* the mixture of substances is emptied into a second hopper *D.* When the bell *E* is lowered the materials drop into the furnace. The use of the two bells and two hoppers makes it possible to prevent the escape of large volumes of gas when the materials are introduced into the furnace. Air heated to  $600^{\circ}$  or  $800^{\circ}$  is now blown into the furnace through tubes *F* called *tuyeres*. The coke burns, the charge melts, the ore is reduced, and the gases which reach the upper part of the furnace contain over 20 per cent of carbon monoxide by volume. These gases escape through a large pipe *J* just below the charging hoppers.

The reduction of the ores is accomplished by the coke or charcoal. The ores are mixed with proper fluxes. The nature of the flux depends upon the ore. If this contains silicon dioxide or clay, lime is added; while, if it contains considerable lime, minerals rich in silicic acid are used, such as feldspar, clay-slate, etc. The object of the flux is to form a slag in which the reduced iron collects, and by which it is protected from oxidation. When the fire is once started in a blast-furnace the operation of reduction is continuous until the furnace is burned out. As the reduced iron collects below, it is from time to time drawn off and allowed to solidify in moulds of sand. The operation requires close attention. The ores must be carefully studied, and the nature and amount of flux regulated according to the character of the ore, as above stated. Then, too, the temperature of the furnace is a matter of

importance, and must be watched, and regulated by means of the blast. The reduction is largely accomplished by carbon monoxide. In the lower part of the furnace the fuel burns to carbon dioxide, but this comes in contact with hot carbon, and is then reduced to the monoxide. The hot monoxide in contact with the oxides of iron reduces these, and is itself converted into the dioxide.

**Varieties of Iron.**—The iron obtained as above described is known as *pig iron* or *cast iron*. It is very impure, containing carbon, phosphorus, sulphur, silicon, etc. If, when drawn from the furnace, the iron is cooled rapidly, a large part of the carbon contained in it remains in chemical combination, and the iron has a silver-white color. This product is known as *white cast iron*. If the iron cools slowly, a large part of the carbon separates as graphite, and this being distributed through the mass gives it a gray color. This product is known as *gray cast iron*. If the ore contains considerable manganese, this is reduced with the iron, and iron made from such ores and containing manganese has the power to take up more carbon than ordinary iron. This product, containing from 3.5 to 6 per cent combined carbon, is known as *spiegeleisen*.

All varieties of pig iron are brittle, and easily fusible. The gray iron fuses at a lower temperature than the white, and is not as brittle; it is therefore well adapted to making castings. When pig iron is treated with hydrochloric acid the carbon which is present in combined form is given off in combination with hydrogen as hydrocarbons, some of which have a disagreeable odor. This is the cause of the bad odor noticed on dissolving ordinary pig iron in acids.

The uncombined or graphitic carbon, on the other hand, remains undissolved. Owing to its brittleness, pig iron cannot be welded. The product of the blast-furnace is always spoken of as pig iron. The general public calls it cast iron. It is the foundation-stone of the iron industry. It is used directly for making kettles and stoves; and it is converted in enormous quantities into wrought iron and steel of many grades.

**Wrought Iron.**—Pig iron and scrap iron are converted into wrought iron by puddling. The puddling-furnace has a flat, oval hearth and a low, arched roof. The sides of the hearth are lined with iron ore (oxide). Coal is burned on a grate, and the flame passes into the furnace at one end and out at the other, thus coming in contact with the roof and the charge of iron. The pig iron is melted, and the carbon and silicon are removed from it, partly by the oxygen of the air, but principally by that in the iron ore which is itself thus reduced to wrought iron.

Wrought iron contains less than 0.5 per cent of carbon, and as the percentage of carbon decreases the malleability increases and the melting-point rises. The melting-point of good wrought iron is from  $1900^{\circ}$  to  $2100^{\circ}$ . Small quantities of sulphur, phosphorus, silicon, and manganese exert a very marked influence upon its properties.

The process of welding consists in heating two pieces of iron to a high temperature, putting some borax upon one of them, laying them together, and hammering, when, as is well known, they adhere firmly together. The object of the borax is to keep the surfaces bright, which it does by uniting with the oxide and forming an easily fusible borate.



**Steel.**—This name was formerly applied to a product intermediate between pig iron and wrought iron so far as the amount of carbon contained in it is concerned. It was made either by taking some of the carbon from pig iron by puddling, or by adding some carbon to wrought iron. At present the name steel is given to the product of the cementation process, and to all products made in the crucible, the converter, or the open-hearth furnace, although these products may differ greatly in composition.

*Open-hearth steel.*—Most of the hard steel in the market to-day is made in the open-hearth furnace. Enormous quantities are used for car springs and agricultural machinery. An open-hearth furnace is one having a hearth exposed to the flame so that any piece of steel or other material placed upon the hearth is exposed to the action of the burning gases. Such a furnace must further be *regenerative*, that is to say, it must be so constructed that the heat carried away in the stack-gases is used to warm the air and gas before they enter the furnace. The open-hearth process may be either an *acid open-hearth process* or a *basic open-hearth process*.

An *acid open-hearth furnace* means a regenerative gas-furnace used for melting steel and lined with sand. In the *acid open-hearth process* a mixture of pig iron and scrap iron is charged into the furnace and melted. Nothing is added to form a slag. The amount of carbon in the steel, and therefore the tensile strength, depends entirely on the conduct of the operation, but the amounts of phosphorus and sulphur depend upon the material put into the furnace.

A *basic open-hearth furnace* is a regenerative gas-furnace, used for melting steel and lined with basic material, usually either magnesite or dolomite (page 408). In

this basic process the charge is composed of pig iron and scrap, together with lime or limestone. This gives a basic slag, that is to say, a slag containing more of the basic material than the silica formed can combine with. Under these circumstances the phosphorus that may be present will be oxidized and enter the slag as phosphate.

Most engineers are of the opinion that open-hearth steel should be used for railway bridges, for boilers, for locomotive forgings, and whenever the steel is subject to vibration and shock.

*Bessemer Steel.*—The Bessemer process is carried out in a converter as shown in Fig. 54. Molten pig iron is poured into this and a blast of air is forced through the molten metal from below, oxidizing the carbon and silicon. No fuel is used, as the heat generated by the oxidation of the carbon and the silicon is sufficient to raise the temperature above  $2100^{\circ}$ . Manganese is added to make the steel tough. If soft steel is wanted, an alloy called *ferro-manganese*, containing 80 per cent of manganese, is used, while if rail-steel is being made, *spiegeleisen* (page 465) is added.

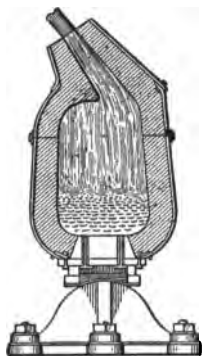


FIG. 54.

In the *acid Bessemer process* the converter is lined with rock and clay rich in silicic acid. There is no removal of phosphorus or sulphur in this process, and as no steel is allowed to contain more than one-tenth of one per cent of either, it is plain that the pig iron must not contain more than this amount. In the *basic Bessemer process* the converter is lined with basic material, usually burned dolomite,

which gives a mixture of magnesia and lime. In such a converter the phosphorus is oxidized as in the acid open-hearth furnace. The basic Bessemer process is not in use in the United States, as the conditions are not favorable. It is often called the Thomas-Gilchrist, or the basic lining process.

Most engineers hold that Bessemer steel will answer for buildings, highway bridges, and similar purposes.

*Crucible Steel.*—This is made by putting into a crucible a mixture of wrought iron and charcoal and heating it until it is thoroughly melted, the crucible being kept tightly closed to prevent the air from entering. This gives a steel free from the minute imperfections often present in open-hearth and Bessemer steel. Such steel is needed for watch-springs, needles, and razors.

*Cementation.*—Wrought iron containing not more than 0.02 per cent of phosphorus may be converted into hard steel by placing it in fine charcoal and exposing it to a yellow heat. The carbon penetrates the iron slowly. The steel thus produced is known as blister or cement steel, and the process is known as cementation.

**Properties of Steel.**—The name steel covers a wide range of products. In general it may be said to be harder than pure iron. If heated very hot and then suddenly cooled by plunging it in water or oil, it becomes very hard and brittle. If heated and then cooled slowly it becomes soft, tough, and elastic. If the hardened steel is reheated to a definite temperature and then properly cooled, almost any required degree of hardness and elasticity can be obtained. This is called *tempering*.

When steel is tempered the product is in a state of unstable equilibrium; the particles are under a strain tending to revert to the condition of the steel before tempering. Constant jarring or even moderate changes of temperature help to hasten this reversion; thus the jarring of an automobile gradually destroys the temper of its steel parts; the frictional heat developed by turning metals on a lathe destroys the temper of the steel-cutting tool.

It has been recently discovered that by alloying steel with large percentages of certain other elements, both metallic and non-metallic, the resulting alloys have according to their composition desirable qualities such as increased hardness or increased toughness, *without tempering*; as these alloys are not tempered they are in a condition of stable equilibrium, and are not affected by jarring or by moderate changes in temperature. All of these new alloys are called "steel," and are technically known as "self-tempered steels."

With this great advance in steel-making, it becomes feasible to find by experiment the best alloy or "steel" for a given purpose, and already many new "steels" are on the market. Two examples will suffice. One of the best "automobile steels" (not affected by the constant jarring and very rigid and tough) contains 40 per cent of nickel. "High speed steels" are steels used for cutting-tools in lathes for turning metals; these new steels are not affected by the frictional heat, thus allowing the lathe to be run at a much higher speed than was possible with tools of ordinary tempered steel. One of the best high-speed steels contains 6 to 7 per cent chromium and 20 to 25 per cent tungsten.

*Use of the electric furnace in modern steel-making.*—The electric furnace is exclusively used in making the ferro-

alloys employed in steel-making, such as ferro-silicon containing 25 to 90 per cent silicon; ferro-chrome with 65 per cent chromium; silico-manganese with 60 to 75 per cent manganese and 20 to 25 per cent silicon; and many others.

To obtain perfect homogeneity in many of these new steels a higher temperature is required than that obtainable by burning coal or gas, and such steels are made in an open-hearth furnace heated by the electric arc.

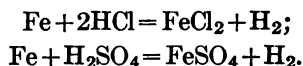
**Uses.**—Every one is familiar with many of the uses of iron. For buildings, rails, steamships, for tools and implements of all kinds, it is practically indispensable. What is called the progress of man is largely dependent upon its use.

About 40 per cent of the world's supply of pig-iron and over 50 per cent of the world's supply of steel are made in the United States. In 1906, 25,307,191 tons of pig-iron and 23,246,251 tons of steel were made in the United States.

**Properties of Iron.**—Pure iron is almost unknown. Of the commercial varieties, it follows from what has been said that wrought iron is the purest. That which is used for piano-strings is the purest commercial iron; it contains only about 0.3 per cent of impurities. Pure iron can be made in the laboratory by igniting the oxide or oxalate in a current of hydrogen, and by reducing ferrous chloride in hydrogen. In larger quantity it can be prepared by melting the purest wrought iron in a lime crucible by means of the oxyhydrogen flame. The impurities are taken up by the crucible, and a regulus of the pure metal is left behind. That made by reduction of the oxide or oxalate is in finely divided condition. If in its preparation the temperature is kept as low as possible, the product known as "iron by

hydrogen " takes fire when brought in contact with the air; while if the temperature is high, the product has not this power. Pure iron is white and is one of the hardest metals. Its melting-point is higher than that of wrought iron. Pure iron is attracted by the magnet. In contact with a magnet or when placed in a coil through which an electric current is passing, it becomes a magnet; but the purer it is the sooner it loses the magnetic power when removed from the magnet or the coil. Steel, however, retains its magnetism. When heated to a sufficiently high temperature iron burns and forms the oxide  $\text{Fe}_3\text{O}_4$ . This takes place much more easily in oxygen than in the air. In dry air iron does not undergo change, but in moist air it *rusts*, or it becomes covered with a layer of oxide and hydroxide which is formed by the action of the air, carbon dioxide, and water. The presence of some salts in solution facilitates the rusting. Various methods are adopted to protect iron from this change, most of which are, however, purely mechanical. A method that promises valuable results is that invented by Barff. This consists in introducing the iron into water-vapor at a temperature of  $650^\circ$ , when it becomes covered with a firmly adhering layer of oxide.

Iron dissolves in acids with evolution of hydrogen, and generally with formation of ferrous salts:



When cold nitric acid is used, ferrous nitrate and ammonium nitrate are the products; if the acid is warmed, ferric nitrate and oxides of nitrogen are formed. When an iron

wire which has been carefully polished is introduced for an instant into red fuming nitric acid it can afterward be put into ordinary nitric acid without undergoing change. It is said to be in the passive state; and the commonly accepted explanation of the phenomenon is that the wire is covered with a thin layer of oxide. As, however, the passive condition is lost by contact with an ordinary wire, the explanation does not appear to be adequate.

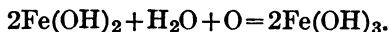
**Iron forms Two Series of Compounds.**—Iron, like mercury, copper, and tin, forms two series of compounds that differ markedly from each other. These are the *ferrous* and *ferric* compounds. Thus with chlorine it forms two chlorides, one of which, *ferrous chloride*, has the composition expressed by the formula  $\text{FeCl}_2$ ; the other, *ferric chloride*, by  $\text{FeCl}_3$ . It appears from a study of the specific gravities of the vapors of these chlorides that the above formulas should be doubled, so that ferrous chloride is now commonly represented by  $\text{Fe}_2\text{Cl}_4$ , and ferric chloride by  $\text{Fe}_2\text{Cl}_6$ .

Similarly there are two oxides,  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$ ; two sulphates, *ferrous sulphate*,  $\text{FeSO}_4$ , and *ferric sulphate*,  $\text{Fe}_2(\text{SO}_4)_3$ , etc.

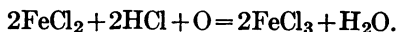
**Ferrous Compounds are Converted into Ferric Compounds by Oxidation.**—Ferrous compounds show a tendency to pass into ferric compounds by simple contact with the air; and are readily converted into these by oxidizing agents, such as nitric acid, potassium chlorate, etc. When, for example, ferrous hydroxide,  $\text{Fe}(\text{OH})_2$ ,\* is exposed to the

\* If ferrous chloride has the formula  $\text{Fe}_2\text{Cl}_4$ , it seems probable that the formula of ferrous hydroxide is  $\text{Fe}_2(\text{OH})_4$ . We have no

air suspended in water, it changes to ferric hydroxide,  $\text{Fe}(\text{OH})_3$ . The change is represented by the equation



So, also, when ferrous chloride is left standing in hydrochloric-acid solution it changes to ferric chloride, and the change is rapidly effected by boiling with a little nitric acid:



**Ferrous chloride**,  $\text{FeCl}_2$ , is formed by dissolving iron in hydrochloric acid.

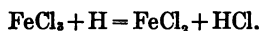
#### FERROUS CHLORIDE AND FERRIC CHLORIDE.

*Experiment 181.*—Dissolve a little iron wire in dilute hydrochloric acid. Hydrogen is evolved, accompanied by small quantities of other gases, the formation of which is due to the presence of impurities in the iron, and carbon is left undissolved as a black residue. To a little of the solution in a test-tube add at once caustic soda. This precipitates ferrous hydroxide,  $\text{Fe}(\text{OH})_2$ , which changes color rapidly. Pure ferrous hydroxide is white. As it passes to the ferric condition it becomes dirty green, and darker and darker until it is reddish brown. Heat another portion of the solution of ferrous chloride to boiling, add two or three drops of concentrated nitric acid, and boil again. Repeat this operation two or three times. The ferrous chloride is thus oxidized to ferric chloride. It will be noticed that the color of the solution after the oxidation is reddish yellow, whereas before the oxidation it was nearly colorless or greenish. Add caustic soda to the solution of ferric chloride. A reddish-brown precipitate of ferric hydroxide will be formed. Just as in this case we

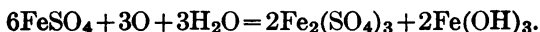
direct evidence bearing upon this, and hence the simpler formula may be used here, particularly as we are for the present interested mainly in the composition of the compound.



have passed from ferrous chloride to ferric chloride by oxidation, so we can pass back again to the ferrous compound. Thus, by adding a little zinc to a solution of ferric chloride in which hydrochloric acid is present, the hydrogen evolved extracts chlorine from the ferric chloride and converts it into ferrous chloride:



**Ferrous Sulphate**,  $\text{FeSO}_4 + 7\text{H}_2\text{O}$ .—This salt, which is commonly known as “green vitriol” or “copperas,” is formed by the action of sulphuric acid on iron. [What is “white vitriol”? (page 417), “blue vitriol”? (page 426).] It undergoes change in the air, being converted into a compound containing ferric sulphate,  $\text{Fe}_2(\text{SO}_4)_3$ , and ferric hydroxide:



Ferrous sulphate (copperas) is used in dyeing, in the preparation of fuming sulphuric acid (see page 302), as a disinfectant, in the manufacture of ink, Prussian blue, and various pigments.

**Iron alum**,  $\text{FeK}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ , is formed by bringing ferric sulphate and potassium sulphate together. It resembles ordinary alum,  $\text{AlK}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ , but differs from it in containing iron instead of aluminium.

**Ferrous oxide**,  $\text{FeO}$ , cannot be prepared pure on account of the ease with which it combines with oxygen.

**Ferric oxide**,  $\text{Fe}_2\text{O}_3$ , occurs in nature in lustrous crystals as *hematite*, and in other valuable ores of iron. The hydroxide corresponding to this—viz., *ferric hydroxide*,  $\text{Fe}(\text{OH})_3$ —

is analogous in composition and properties to aluminium hydroxide. It is a weak base, but, unlike aluminium hydroxide, it does not form compounds with bases (see page 448). Hence it does not dissolve in caustic soda and caustic potash. [Try it. Suppose a solution contains an aluminium salt and a ferric salt, and caustic soda is added, what will first take place? If more is added and the solution filtered, where will the aluminium be found, and where the iron?]

Certain natural compounds of iron appear to be derivatives of the hydroxide  $\text{FeO.OH}$ , which corresponds in composition to the aluminium compound  $\text{AlO.OH}$ , and to metaboric acid,  $\text{BO.OH}$ . Thus magnetite is believed to be the ferrous salt of this acid as represented by the formula

$\frac{\text{FeO.O}}{\text{FeO.O}} > \text{Fe}$ ; and franklinite is probably the corresponding

zinc salt  $\frac{\text{FeO.O}}{\text{FeO.O}} > \text{Zn}$ .

**Ferroso-ferric oxide**,  $\text{Fe}_3\text{O}_4$ , or magnetic oxide of iron, is found in nature in the form of loadstone. It is formed when iron is burned in oxygen (see Experiment 24, page 31).

**Ferric Acid**,  $\text{H}_2\text{FeO}_4$ .—It is interesting to note that iron combines with a larger proportion of oxygen than is contained in any of the compounds of that metal thus far mentioned, and then forms an acid. Potassium ferrate has the composition represented by the formula  $\text{K}_2\text{FeO}_4$ .

**Sulphides of Iron**.—The *sulphides* of iron have been repeatedly mentioned. *Ferrous sulphide*,  $\text{FeS}$ , is made by heating sulphur and iron together in proper proportions. It is used in making hydrogen sulphide. [Explain how.]

**Iron pyrites, or pyrite**,  $\text{FeS}_2$ , is a yellow crystallized sub-

stance which is widely and abundantly distributed in nature. When heated in a closed tube, sulphur is given off. When heated in an open vessel, as upon a shallow iron pan, the sulphur is oxidized to sulphur dioxide, and the iron is left in the form of the oxide. [Verify these statements by experiment.]

**Nickel**, Ni (At. Wt. 59), is found in meteoric iron and in combination with arsenic. It forms two series of salts corresponding to the two hydroxides, nickelous hydroxide,  $\text{Ni(OH)}_2$ , and nickelic hydroxide,  $\text{Ni(OH)}_3$ .

Most nickel salts are colored green.

Alloys of nickel are extensively used. *Argentan*, or *German silver*, consists of copper, zinc, and nickel. Various nickel alloys are used for making coins. The 5- and 3-cent pieces of the United States are made of an alloy consisting of 25 per cent nickel and 75 per cent copper.

Nickel is extensively used at present in nickel plating. Iron objects are covered with a thin layer of the metal for the purpose of protecting them from rusting. The plating is carried out in the same way as silver plating and copper plating are—by means of electrolysis—a bath of nickel-ammonium sulphate being used. Much nickel is used in making nickel steel.

Nickel is, further, extensively used in nickel plating. Iron is covered with a thin layer of the metal to protect it from rusting.

**Cobalt**, Co (At. Wt. 59), is found in combination with arsenic and sulphur, and also in small quantities accompanying nickel in meteoric iron.

The salts of cobalt are red in combination with water, and blue when dried. If marks are made on paper with a dilute solution of one of its salts, the color is not perceptible. If, however, the paper is held before a fire, the salt loses water and turns blue, and, as the blue is more intense than the red, it is visible. When the salt is again moistened it becomes invisible. This is the basis of the preparation of the so-called *sympathetic inks*.

**Smalt.**—The beautiful pigment known by this name is essentially a cobalt glass in which cobalt takes the place of calcium. It is made by heating compounds of cobalt with quartz and potassium carbonate. The glass thus formed is powdered very finely and used as a pigment. It does not change color in the sunlight, and is not affected by acids or by alkalies.

## CHAPTER XXVII.

### MANGANESE.—CHROMIUM.—URANIUM.

**Manganese, Mn** (At. Wt. 55).—Manganese is found in nature in the form of oxides, of which manganese dioxide, or the black oxide of manganese, occurs most abundantly. By treating ores containing manganese and iron in the blast furnace or electric furnace, the alloys "spiegel-eisen" and ferro-manganese are made. These alloys are used in great quantities in making Bessemer steel and the modern steels.

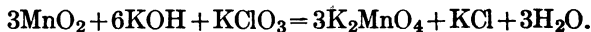
**Compounds of Manganese with Oxygen.**—With oxygen it forms the following compounds: *Manganous oxide*,  $\text{MnO}$ ; *manganic oxide*,  $\text{Mn}_2\text{O}_3$ ; *manganoso-manganic oxide*,  $\text{Mn}_3\text{O}_4$ ; *manganese dioxide*,  $\text{MnO}_2$ ; and *permanganic anhydride*,  $\text{Mn}_2\text{O}_7$ .

**Comparison of Manganese with Aluminium and with Iron.**—Manganese presents points of resemblance with aluminium and iron. Like iron it forms two series of salts, the manganous and manganic series, which differ from each other very much as ferrous and ferric salts do. Like iron, also, it forms an oxide,  $\text{Mn}_3\text{O}_4$ , which is analogous to the magnetic oxide of iron. Unlike iron, it forms the dioxide  $\text{MnO}_2$ . Like iron, it forms salts, which are derived from an acid of the formula  $\text{H}_2\text{MnO}_4$ ; as, for example, *potassium manganate*,  $\text{K}_2\text{MnO}_4$ . Unlike iron, it forms salts derived from an acid,  $\text{HMnO}_4$ ; as, for example, *potassium permanganate*,  $\text{KMnO}_4$ .

**Formation of Manganous Salts.**—The higher oxides of manganese generally yield manganous salts when heated with the ordinary acids, the action being accompanied by loss of oxygen. In these salts the metal is apparently bivalent. The use of manganese dioxide in preparing oxygen (page 100) and chlorine (page 111) has been described. [Give an account of the changes which manganese dioxide undergoes when treated with sulphuric acid; hydrochloric acid; when heated.]

**Manganese Dioxide,  $MnO_2$ .**—This important compound occurs in nature in considerable quantity, and is known as pyrolusite or black oxide of manganese. The chief application of the dioxide is in the preparation of chlorine. It is also used for making oxygen, and for the purpose of decolorizing glass. In the last process a small quantity is added to the molten glass. This alone would give the glass an amethyst color. Without it the glass would be green. One color counteracts the other, and the glass appears colorless.

**Potassium Permanganate,  $KMnO_4$ .**—This salt is obtained from potassium manganate,  $K_2MnO_4$ , by boiling its solution in water or by passing carbon dioxide into such a solution. The manganate is made by treating manganese dioxide with potassium hydroxide and potassium chlorate; in other words, by oxidizing manganese dioxide in the presence of the base, potassium hydroxide. The reaction is represented by the equation



The permanganate is a dark-colored, crystallized compound that dissolves in water, forming a deep purple solution.

## PREPARATION OF POTASSIUM PERMANGANATE.

*Experiment 182.*—In a porcelain crucible heat 5 grams powdered manganese dioxide, 5 grams potassium hydroxide, and  $2\frac{1}{2}$  grams potassium chlorate. When the mass has turned green, let it cool, dissolve in water, neutralize most of the alkali, and boil. The green substance is potassium manganate. The color will change from green to purple.

**Reduction of Potassium Permanganate.**—Potassium permanganate gives up its oxygen very readily and changes to a hydroxide of manganese. If an acid is present the hydroxide dissolves, forming a colorless solution. When, therefore, a solution of potassium permanganate is added to an acid solution containing an oxidizable substance it becomes colorless.

## OXIDATION BY MEANS OF POTASSIUM PERMANGANATE.

*Experiment 183.*—To a dilute solution of ferrous sulphate containing free sulphuric acid add drop by drop a dilute solution of potassium permanganate. The color will be destroyed as long as there is any ferrous sulphate present.

Add some permanganate solution to a solution of sulphur dioxide in water. [What would you expect to take place in this case?]

Add some comparatively dilute hydrochloric acid to a few crystals of potassium permanganate in a test-tube. [What do you notice? How do you explain the change?]

**Comparison of Potassium Permanganate with Potassium Perchlorate.**—Potassium permanganate,  $\text{KMnO}_4$ , is analogous to potassium perchlorate,  $\text{KClO}_4$ , not only in composition, but in its general properties.

**Chromium, Cr (At. Wt. 52).**—This element is comparatively rare, and occurs almost always in combination with

oxygen and iron as chromic iron. This mineral, whose composition is represented by the formula  $\text{FeCr}_2\text{O}_4$ , may be regarded as the iron salt of an acid of the formula  $\text{HCrO}_2$ . Replacing two atoms of hydrogen of this acid by one of iron, we should have a compound  $\text{Fe}(\text{CrO}_2)_2$ . This is analogous to spinel, which in a similar way is regarded as magnesium aluminate of the formula  $\text{Mg}(\text{AlO}_2)_2$ . Chromium is used in the manufacture of "chrome steel."

**Compounds of Chromium.**—The principal compounds of chromium with which we have to deal are *potassium chromate*,  $\text{K}_2\text{CrO}_4$ ; *potassium bichromate*,  $\text{K}_2\text{Cr}_2\text{O}_7$ , and other salts derived from chromic acid. There are, however, salts in which chromium takes the part of a metal, replacing the hydrogen of acids; as, for example, *chromium sulphate*,  $\text{Cr}_2(\text{SO}_4)_3$ .

**Potassium chromate**,  $\text{K}_2\text{CrO}_4$ , is formed when finely powdered chromic iron is heated with potassium carbonate and potassium nitrate.

#### PREPARATION OF POTASSIUM CHROMATE.

*Experiment 184.*—Powder some chromic iron very fine. Mix 3 grams each of potassium hydroxide, potassium carbonate, and potassium nitrate. Melt in an iron crucible, using the blast-lamp, and add the chromic iron a little at a time, as long as it dissolves. After cooling treat the mass with water, when a yellow-colored solution will be formed. Potassium chromate is in the solution. Save this.

**Potassium Bichromate**,  $\text{K}_2\text{Cr}_2\text{O}_7$ .—This is the form in which chromium is most frequently met with. It is made from the chromate by adding acetic or nitric acid, and forms



large red crystals that are soluble in water. The change is represented thus:



The relation between the chromate and the bichromate will be more readily understood by considering the acids from which they are derived. These are chromic acid,  $\text{H}_2\text{CrO}_4$ , and bichromic acid,  $\text{H}_2\text{Cr}_2\text{O}_7$ . The latter may be regarded as derived from the former by loss of water:

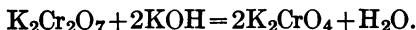


The same relation exists between sulphuric acid,  $\text{H}_2\text{SO}_4$ , and disulphuric or fuming sulphuric acid,  $\text{H}_2\text{S}_2\text{O}_7$ .

#### FORMATION OF POTASSIUM BICHROMATE FROM POTASSIUM CHROMATE.

*Experiment 185.*—Concentrate the solution of potassium chromate already obtained and add nitric acid enough to decompose the unused potassium carbonate and give the solution an acid reaction. The color will change from yellow to red. The red color indicates the presence of the bichromate.

When a solution of potassium bichromate is treated with potassium hydroxide until the color becomes pure yellow the chromate is formed:



#### CONVERSION OF POTASSIUM BICHROMATE INTO POTASSIUM CHROMATE.

*Experiment 186.*—Convert 10 to 20 grams potassium bichromate into the chromate by the method mentioned. Evaporate to crystallization.

**The Chromate and Bichromate are Good Oxidizing Agents.**—Both the chromate and the bichromate are good oxidizing agents.

**Insoluble Chromates.**—The chromates of barium and lead, like the sulphates, are insoluble in water. They are yellow. Lead chromate is the well-known pigment *chrome-yellow*.

#### PRECIPITATION OF INSOLUBLE CHROMATES.

*Experiment 187.*—Add a little of a solution of potassium chromate or bichromate to a solution of a barium salt and of a lead salt.

**Chrome Alum** is a salt allied to ordinary alum, but containing chromium instead of aluminium. Its formula is  $\text{CrK}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ . All alums have analogous formulas:

Ordinary alum. ....	$\text{AlK}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$
Iron alum. ....	$\text{FeK}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$
Chrome alum. ....	$\text{CrK}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$

As has been explained, alum (see page 443) is a compound of aluminium sulphate and the sulphate of one of the alkali metals, generally potassium. Similarly ferric sulphate combines with the sulphates of the alkali metals, forming the iron or ferric alums, such as  $\text{FeK}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ ,  $\text{FeNa}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ , etc. Chromium sulphate acts in the same way as aluminium and ferric sulphates.

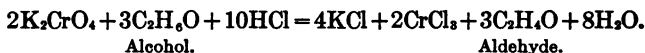
**Comparison of Chromium with Aluminium, Iron, and Sulphur.**—In its general chemical conduct chromium is similar to aluminium and iron on the one hand; while on the other hand its resemblance to sulphur is unmistakable, as is seen in the formation of the acids, chromic and bi-

chromic acids, which are analogous to sulphuric and disulphuric acids, not only in composition, but in some of their properties. [Are the lead and barium salts of sulphuric acid soluble or insoluble in water?]

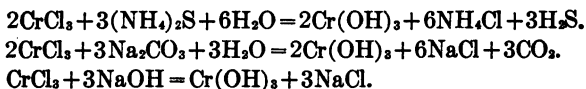
In its conduct towards reagents chromium more closely resembles aluminium than iron. It forms no sulphide and no carbonate, so that when a soluble carbonate or sulphide is added to a solution of a chromium salt, such as chrome alum, the hydroxide is precipitated, as in the case of aluminium. The hydroxide dissolves in caustic soda and caustic potash, but is reprecipitated when the solution is boiled. [How do aluminium and iron hydroxides act towards caustic soda?]

#### REACTIONS OF CHROMIUM AS SHOWN BY CHROMIC SALTS.

*Experiment 188.*—To a solution of potassium chromate add some rather strong hydrochloric acid and a little alcohol. On boiling, the alcohol takes up oxygen from the chromate, a peculiar-smelling substance, aldehyde, is given off, and the solution now contains chromic chloride,  $\text{CrCl}_3$ . The solution has a green color. The change is represented thus:



To separate portions of the diluted solution add ammonium sulphide, sodium carbonate, and sodium hydroxide. The reactions which take place are:



After noticing the general appearance of the precipitate formed with caustic soda, add an excess of the latter. [Does the precipitate dissolve?] Boil the solution. [What takes place?]

**Uranium**, U (At. Wt. 240).—This element occurs mostly in the form of the oxide  $\text{U}_3\text{O}_8$  known as pitch-blende. It forms salts in which the group  $\text{UO}_2$ , called *uranyl*, takes the place of two atoms of hydrogen: as, for example, *uranyl nitrate*,  $\text{UO}_2(\text{NO}_3)_2$ ; *uranyl sulphate*,  $\text{UO}_2(\text{SO}_4)$ .

Uranium oxide,  $\text{U}_2\text{O}_3$ , conducts itself towards bases like an acid, forming salts called uranates.

**Radium**.—Certain products obtained in very small quantities from pitch-blende give off rays that in some respects resemble the Roentgen rays, but in other respects differ from them. These rays pass through opaque bodies and afterwards produce impressions upon photographic plates and they act upon the air, making it a conductor of electricity. The most important of these substances is the remarkable element radium. This is now being actively investigated. It has been found to give off several different kinds of rays and a substance in the form of an emanation. All these produce characteristic effects by means of which they can be recognized.

The emanation given off by radium is unstable, and it yields helium as one of the products of its spontaneous decomposition. This is the only example known of the formation of one element from another.

## CHAPTER XXVIII.

### PALLADIUM.—PLATINUM.—GOLD.

**Palladium** forms with hydrogen a compound which in general has the properties of alloys. It has the composition  $\text{Pd}_2\text{H}$ , and contains about 600 volumes of hydrogen to 1 volume of palladium. The properties of this substance have led to the view that hydrogen has metallic properties. If by the name metal is meant an element that forms salts with acids, then it may be said that hydrogen bears to other metals a relation similar to that which carbonic acid bears to other acids. Acids are simply salts of hydrogen, and other metals drive out the hydrogen. Carbonates are in the same way decomposed by all other acids. The study of liquid hydrogen has, however, shown that this element has nothing in common with the metals.

**Platinum**, Pt (At. Wt. 195), occurs almost always accompanied by iridium, palladium, rhodium, ruthenium, and osmium, in the form of alloys. The ore is found in the Ural Mountains, in California, Australia, and a few other places. It is prepared by treating the ore with strong *aqua regia*, which dissolves the platinum, together with some iridium. The chlorplatinic acid,  $\text{H}_2\text{PtCl}_6$ , thus obtained is precipitated by means of ammonium chloride, with which, as with potas-

sium chloride (see page 380), it forms a difficultly soluble compound,  $(\text{NH}_4)_2\text{PtCl}_6$ . When this is heated to a sufficiently high temperature it is decomposed, leaving metallic platinum as a residue. By special methods the iridium can be separated from it.

**Properties.**—Platinum is a grayish-white metal with a high lustre. Its specific gravity is 21.15, it being one of the heaviest substances known. The specific gravity of iron is 7.8, that of lead 11.4, and that of lithium 0.59 (see page 176). In other words, a piece of platinum weighs nearly three times as much as a piece of iron of the same dimensions, and nearly twice as much as a piece of lead of the same dimensions. Platinum is not dissolved by hydrochloric, nitric, or sulphuric acid; but *aqua regia* dissolves it, forming chlorplatinic acid,  $\text{H}_2\text{PtCl}_6$ . Fusing caustic alkalies attack it; sodium carbonate does not. It does not change in the air, and does not melt except in the flame of the oxyhydrogen blowpipe or electric furnace. It resists the action of most substances. These properties make it extremely valuable to the chemist. Platinum crucibles and evaporating-dishes, foil, and wire are constantly used in the laboratory, and it is difficult to see how we could get along without them. Large retorts of platinum are used for the purpose of concentrating sulphuric acid and distilling it.

**Alloys of Platinum.**—The only alloy of platinum of importance is that which it forms with iridium. A small percentage of this metal diminishes the malleability of platinum very markedly and makes it brittle, but increases its power of resistance to the action of reagents. An alloy of 90 per cent platinum and 10 per cent iridium has been

adopted by the French Government as the best material from which to make normal meters. This alloy is very hard, as elastic as steel, more difficultly fusible than platinum, entirely unchangeable in the air, and is capable of a high polish.

**Chlorplatinic Acid**,  $\text{H}_2\text{PtCl}_6$ , is made by dissolving platinum in *aqua regia* and evaporating off the acids. It dissolves in water, forming a yellowish-red solution, which is used in the laboratory for the purpose of precipitating potassium from its solutions, as the salt *potassium chlorplatinite*,  $\text{K}_2\text{PtCl}_6$ , is difficultly soluble in water. The corresponding sodium salt,  $\text{Na}_2\text{PtCl}_6 + 6\text{H}_2\text{O}$ , is easily soluble in water.

**Gold**, Au (At. Wt. 197).—According to the arrangement of the elements in the periodic system gold falls in the same group with copper and silver, with which it has some points of resemblance. It forms more properly the connecting link between the platinum group and the members of the second and third groups.

**Forms in which Gold occurs in Nature.**—Gold is generally found in nature in the native or uncombined condition—a fact which is undoubtedly due to its chemical inactivity. That which is found in nature is never pure, but contains silver, and also, in different localities, iron, copper, and other metals. It is also found to some extent in combination with tellurium in the compounds  $\text{AuTe}_2$  and  $(\text{AuAg})_2\text{Te}_3$ . Native gold is frequently found enclosed in quartz, or more commonly in quartz sand. The principal localities in which it is found are California and some of the other Western States, and Australia, Hungary, Siberia, and Africa.

**Metallurgy of Gold.**—From the chemical point of view the metallurgy of gold is in general very simple. There are two kinds of gold-mining—called *placer \*-mining* and *vein-mining*. In the former the earth and sand that contain gold are washed with water, which carries away the lighter particles and leaves the gold mixed with other heavy materials. This mixture is then treated with mercury, which forms an amalgam with the gold, as it does with silver, and when this is placed in a retort and heated, the mercury passes over, leaving the gold behind. If silver is present, as is frequently the case, this is separated with the gold. In *vein-mining* the gold ores are taken out of veins in the earth and the gold separated by grinding the ores and treating them with mercury, as in the last stage of *placer-mining*. *Hydraulic mining* is a modification of ordinary *placer-mining*. It consists in forcing water under pressure against the sides of hills and mountains in which gold occurs loosely mixed with the earth. The earth is thus carried away and the heavier gold is deposited in sluices.

From the ores gold can be extracted by chlorine and by potassium cyanide.

The *chlorination process* consists in subjecting the finely divided ore in suspension in water to the action of chlorine from bleaching-powder. From the solution thus obtained the gold is precipitated in the metallic form.

The *cyanide process* is based upon the fact that gold in finely divided condition dissolves in a solution of potassium cyanide. From the solution the gold can be separated by zinc or electrolytically.

The gold obtained as above is not pure. It can be sepa-

\* Pronounced pläs'-er.



rated from silver by dissolving it in *aqua regia*, evaporating so as to drive off the nitric acid, then diluting, and treating with a reducing agent, when metallic gold is precipitated. Thus when ferrous sulphate is used the following reaction takes place:



Another method of separating silver from an alloy with gold consists in treating the metal with nitric acid or with boiling concentrated sulphuric acid, which dissolves the silver and leaves the gold. This process is not satisfactory, however, unless the amount of gold in the alloy is less than 25 per cent. If there is more gold than this present the silver is not completely dissolved. If the proportion of gold is greater than this, the alloy is melted with silver enough to bring the percentage of gold down to that mentioned. This is known as *quartation*. Pure gold is now generally obtained by electrolysis.

**Properties.**—Gold is a yellow metal with a high lustre. It is quite soft and extremely malleable, so that it is possible to make from it sheets the thickness of which is not more than 0.000002 millimetre. Thin sheets are translucent, and the transmitted light appears green. Its specific gravity is 19.3; its melting-point higher than that of copper, being about 1200°. It crystallizes in the regular system. Gold combines directly with chlorine, but not with oxygen. The three acids, hydrochloric, nitric, and sulphuric, do not act upon it; but *aqua regia* dissolves it, forming chlorauric acid,  $\text{HAuCl}_4$ . Molten caustic alkalies and their nitrates act upon it, probably in consequence of the tendency to form aurates.

**Alloys of Gold.**—The principal alloy of gold is that which it forms with copper. The standard gold coin of the United States contains nine parts of gold to one of copper. The composition of gold used for jewelry is usually stated in terms of carats. Pure gold is 24-carat gold; 20-carat gold contains 20 parts of gold and 4 parts of copper; 18-carat gold contains 18 parts of gold and 6 parts of copper, etc. Copper gives gold a reddish color, and makes it harder and more easily fusible. Gold is also alloyed with silver; and the alloy with mercury, known as gold-amalgam, is extensively used in the processes for extracting gold from its ores.

**Production of Gold and Silver.**—The figures for the production of gold and silver for the last hundred years are interesting.

*Yearly average production of gold and silver in metric tons (1000 kilograms).*

Year	Gold	Silver
1800-1850.....	24.....	655
1851-1880.....	188.....	1422
1881-1890.....	158.....	3125
1891-1895.....	245.....	4901
1896-1900.....	387.....	5153
1901-1905.....	485.....	5197

An average of the last few years gives as the value of the gold \$350,000,000; of the silver, \$100,000,000.

Formerly most of the gold and silver was used for coinage. Now both are largely used for other purposes.

*Use of gold for coinage and industrial purposes in tons.*

Year	Coinage	Industrial Purposes
1831-1850.....	42.....	19
1851-1870.....	32.....	32
1871-1880.....	73.....	41
1881-1885.....	23.....	70

At present it is estimated that 100-120 tons of gold yearly are used for industrial purposes, notably for jewelry, for gold-plated objects, for dentistry, for photography, for stained glass, and for gilding porcelain and glass. Fifteen tons of gold yearly are used for the latter purpose alone.

*Gold production by countries for 1906, in tons.*

Australasia, 124; Africa, 203; United States, 142. Total including other countries, 602. As will be seen, Africa at present leads the world.

**Chlorides of Gold.**—*Auric chloride*,  $\text{AuCl}_3$ , is formed by heating gold in chlorine. If this is heated in an atmosphere of carbon dioxide, it is decomposed into *aurous chloride*,  $\text{AuCl}$ , and chlorine. When treated with a solution of stannous chloride a solution of auric chloride gives a purple-colored precipitate, known as the *purple of Cassius*, which appears to consist of finely divided gold.

## CHAPTER XXIX.

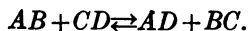
### OSMOTIC PRESSURE.—EQUILIBRIUM.—LAW OF MASS ACTION.

**Osmotic Pressure.**—When a vessel filled with alcohol and tightly covered by a piece of bladder tied over its mouth is immersed in water the bladder is soon stretched outward, showing that liquid from without has found its way through the bladder into the vessel. The simplest phenomenon of this kind is seen when a wide glass tube, tightly closed with a piece of bladder at the lower end, is partly filled with alcohol and then placed in a vessel of water, so that the level of the alcohol inside the tube is the same as that of the water outside. If the tube is fixed in this position, the liquid is soon found to rise in the tube. There is pressure from without inward. This is called *osmotic pressure*. This subject has been under active investigation of late years. Methods of measuring osmotic pressure have been perfected, and it is now possible to make accurate measurements of this kind of pressure with comparative ease. The membrane employed is no longer a piece of bladder, but a fine porous clay cell in the pores of which copper ferrocyanide has been deposited.

The laws of osmotic pressure are similar to the laws of

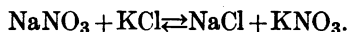
gases. The law of chief importance to chemistry is this: *Quantities of dissolved substances which are in the ratio of the molecular weights of these substances exert equal pressures at the same temperatures if the volume of their solutions is the same.* This being established it plainly furnishes the basis of a method for determining the molecular weights of substances in solution.

**Equilibrium.**—In every case in which two compounds act upon each other chemically to form two new ones several forces must be at work. Suppose, for example, two compounds  $AB$  and  $CD$ , both gases, act upon each other to form two compounds  $BC$  and  $AD$ , also both gases. The simplest course of such a reaction would lead to the formation not only of the two compounds  $BC$  and  $AD$ , but  $AB$  and  $CD$  would also be present in the resulting system. For  $A$  tends to combine with  $B$  as well as with  $D$ , and  $C$  tends to combine with  $D$  as well as with  $B$ . All these tendencies come into play when the two compounds  $AB$  and  $CD$  are brought together, and also when the compounds  $BC$  and  $AD$  are brought together. The result is an *equilibrium* between the four compounds. This may be represented thus:

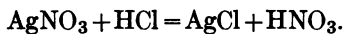


This indicates that the reaction may proceed in either direction—that, in fact, it does proceed in both directions. When the reaction in one direction is equal to the reaction in the other direction equilibrium is reached. This same kind of equilibrium is established also in those cases in which soluble substances act upon each other in solution to form products that are soluble. Thus sodium nitrate and potassium

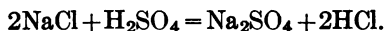
chloride are both soluble in water, and if they react with each other they form sodium chloride and potassium nitrate, both of which are also soluble in water. In fact they do react with the formation of these substances, but if enough water is employed the products remain in solution, and they react with each other to form sodium nitrate and potassium chloride. The equation representing the action is an equilibrium equation:



Most ordinary reactions that we have to deal with are not equilibrium reactions. Thus when hydrochloric acid in solution acts upon silver nitrate in solution the reaction takes place as represented in this equation:

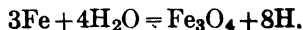


One of the products, the silver chloride, is insoluble in water, is precipitated, and is thus removed from the field of action. So also when sulphuric acid acts upon sodium chloride the reaction takes place thus:

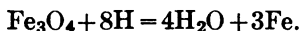


In this case one of the products, the hydrochloric acid, is a gas, and it therefore escapes from the field of action, the sodium sulphate being left behind.

**Mass Action.**—When water vapor is passed over heated iron the water is decomposed by the iron, and hydrogen and a compound of iron and oxygen are formed (see pages 47 and 103). The action is represented thus:



On the other hand, when hydrogen is passed over heated oxide of iron the oxide is reduced (see page 471), and water and metallic iron are formed as represented in the equation



The two reactions here referred to are the reverse of each other. One reason why the two are possible is found in the proportions in which the substances react in the two cases.

In the first case the water is always present in large excess and as soon as any hydrogen is formed this is carried away and cannot under the circumstances act upon the oxide of iron. Therefore the reaction takes place continuously in the direction indicated.

In the second case hydrogen is always present in large excess, and as soon as any water is formed by its action upon the oxide this water is carried away and the reaction proceeds in the direction indicated.

These two reactions illustrate the influence of the relative quantities of reacting substances upon the course of the reactions. This is called *mass action*. An important law has been discovered which expresses the influence of mass in chemical reactions. This is known as the *law of mass action*.

## CHAPTER XXX.

### SOME FAMILIAR COMPOUNDS OF CARBON.

**Organic Chemistry.**—When the compounds that are obtained from plants and animals were first studied, they were supposed to be entirely different from the compounds obtained from the inorganic, or mineral, constituents of the earth. The former were called *organic compounds* because they were obtained from organized things, while the latter were called *inorganic compounds*. Organic compounds were the subject of *Organic Chemistry*, and inorganic compounds formed the subject of *Inorganic Chemistry*. These names are still in use, though they have lost their original significance. Organic Chemistry now means only the *Chemistry of the Compounds of Carbon*.

**Occurrence of the Compounds of Carbon.**—The compound of carbon that occurs most widely distributed in nature is carbon dioxide. This, as has been pointed out, is the starting-point of all life on the globe. All living things are formed from it either directly or indirectly. Attention has been called to the fact that starch and cellulose are the principal compounds found in plants, and that fats, albumin, and fibrin are the most common substances found in animals.



**Formation of Hydrocarbons.**—Certain natural processes which are not thoroughly understood have given rise to the formation of a complex mixture of organic compounds, principally hydrocarbons, in *petroleum*. One of the processes involved in the formation of these hydrocarbons appears to be the action of water on metallic carbides (see Marsh-gas or Methane, page 503).

**Distillation of Coal.**—The destructive distillation of coal for the purpose of making illuminating-gas (page 242) and the formation of *coal-tar* (page 217) have already been referred to. Coal-tar is one of the most important sources of compounds of carbon (page 218). The hydrocarbons benzene,  $C_6H_6$ , toluene,  $C_7H_8$ , xylene,  $C_8H_{10}$ , naphthalene,  $C_{10}H_8$ , anthracene,  $C_{14}H_{10}$ , etc., are obtained from this source.

**Distillation of Wood.**—Wood is heated in closed vessels mostly for the purpose of making charcoal, as already explained. Among the products obtained from this source are *wood-spirit*, or *methyl alcohol*, and *pyroligneous acid*, or *acetic acid*. Large quantities of acetic acid are prepared in this way.

**Distillation of Bones.**—In order to make bone-black, bones are heated in retorts until liquid no longer passes over. This process is called "destructive distillation," as it involves the decomposition of the organic substances of the bones. The oil which passes over is collected and known as *bone-oil*. This is the source of a large number of compounds which are of special interest on account of their connection with the valuable alkaloids quinine, morphine, etc.

**Fermentation.**—A number of the most important compounds of carbon are formed by a process known as *fermentation*. This is a general term meaning any process in which a chemical change is effected by means of minute animal or vegetable organisms. The best-known example of fermentation is that of sugar, which gives rise to the formation of ordinary *alcohol*.

**Classes of Compounds of Carbon.**—The chief classes of these compounds are the *hydrocarbons*; the *alcohols*; the *aldehydes*; the *acids*; the *ethers*; and the *ethereal salts*. First a few of the best-known examples of each of these classes will be taken up, and afterwards some other familiar compounds which do not belong to any one of these classes.

#### HYDROCARBONS.

**Compounds of Carbon and Hydrogen.**—It is not an easy matter to effect combination between carbon and hydrogen in the laboratory except in a few simple cases. In nature processes are in operation which give rise to the formation of a large number of compounds containing these elements; and, further, in the manufacture of illuminating-gas from coal the conditions are such as to cause the combination of carbon and hydrogen, several interesting compounds being thus formed. There are no other two elements which combine with each other in as many different proportions as carbon and hydrogen. The compounds thus formed are known as *hydrocarbons*. The number of hydrocarbons known is very great, being about two hundred. Fortunately, investigation has shown that quite simple relations exist between these compounds; and hence, though the

number is large, the study is not as difficult as might be expected.

**Petroleum** is an oily liquid found in many places in the earth in large quantity, particularly in Pennsylvania, West Virginia, Ohio, Texas, California, and the Caucasus. In the earth it contains gases and liquids. When it is brought into the air, the pressure being removed, the gases are given off. There are several gaseous hydrocarbons given off and a large number of liquids left behind.

**Refining of Petroleum.**—The vapors from petroleum when mixed with air are explosive, and the thicker liquids clog the lamps and wicks. Therefore these must be removed before the oil is fit for household use. This is done by (1) distilling, (2) washing with sulphuric acid, (3) washing with alkali, and (4) washing with water. The product thus prepared is called *kerosene*.

In refining petroleum a number of products are obtained which cannot be used in lamps. Those which are lighter than kerosene, that is to say those which boil at a lower temperature, are known as *gasoline*, *naphtha*, *benzine*, etc. From the heavier portions, or those which boil at higher temperatures than kerosene, *lubricating oils* and *paraffin* are made. Each of these substances is a mixture of several chemical compounds.

**Hydrocarbons Contained in Petroleum.**—The simplest hydrocarbon contained in petroleum is methane, or marsh-gas,  $\text{CH}_4$ ; the next has the composition  $\text{C}_2\text{H}_6$ , the next  $\text{C}_3\text{H}_8$ , etc. It will be seen that, as far as composition is concerned, these compounds bear a simple relation to one

another. They are the first members of a series the names and symbols of the first eight members of which are given below.

$\text{CH}_4$ , Methane, or Marsh-gas;  
 $\text{C}_2\text{H}_6$ , Ethane;  
 $\text{C}_3\text{H}_8$ , Propane;  
 $\text{C}_4\text{H}_{10}$ , Butane;  
 $\text{C}_5\text{H}_{12}$ , Pentane;  
 $\text{C}_6\text{H}_{14}$ , Hexane;  
 $\text{C}_7\text{H}_{16}$ , Heptane;  
 $\text{C}_8\text{H}_{18}$ , Octane.

**Homology.**—The first member of the series differs from the second by  $\text{CH}_2$ ; there is the same difference between any two consecutive members of the series. This relation is known as *homology*, and such a series is called an *homologous series*. Carbon is distinguished from all other elements by its power to form homologous series.

**The Ethylene Series of Hydrocarbons.**—Besides the series above mentioned, which is known as the *marsh-gas series*, there are other homologous series of hydrocarbons. There is one beginning with ethylene,  $\text{C}_2\text{H}_4$ , examples of which are

Ethylene,  $\text{C}_2\text{H}_4$ ;  
Propylene,  $\text{C}_3\text{H}_6$ ;  
Butylene,  $\text{C}_4\text{H}_8$ .

**The Acetylene Series.**—There is a series beginning with acetylene, examples of which are

Acetylene,  $\text{C}_2\text{H}_2$ ;  
Allylene,  $\text{C}_3\text{H}_4$ .

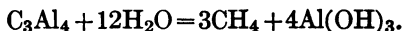
**The Benzene Series.**—Another series begins with benzene,  $C_6H_6$ . Some of the members of this series are

Benzene,  $C_6H_6$ ;

Toluene,  $C_7H_8$ ;

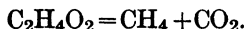
Xylene,  $C_8H_{10}$ .

**Marsh-gas, Methane, Fire-damp,  $CH_4$ .**—Marsh-gas is found in nature in petroleum, and is given off when the oil is taken out of the earth and the pressure is removed. It is formed, as the name implies, in marshes, as the product of a reducing process. Vegetable matter is largely composed of carbon, hydrogen, and oxygen. When it undergoes decomposition in the air in a free supply of oxygen, the final products formed are carbon dioxide and water. When the decomposition takes place without access of oxygen, as under water, marsh-gas, which is a reduction-product, is formed. The gas can be made by treating aluminium carbide,  $C_3Al_4$ , with water:



Marsh-gas is met with in coal-mines, and is known to the miners as *fire-damp*. “Damp” being the general name applied to a gas, the name fire-damp means a gas that burns. To prepare it in the laboratory, it is most convenient to heat a mixture of sodium acetate and quicklime. The change which takes place will be most readily understood by considering it as a simple decomposition of acetic acid. Acetic acid has the formula  $C_2H_4O_2$ . When heated alone, it boils and does not suffer decomposition. If it is converted into a

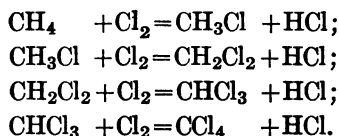
salt, and heated in the presence of a base, it breaks up into marsh-gas and carbon dioxide:



As the carbon dioxide forms salts with bases it does not pass off, but remains behind in the form of a salt as a carbonate.

Marsh-gas is a colorless, transparent, tasteless, inodorous gas. It is slightly soluble in water. It burns, forming carbon dioxide and water. When mixed with air, the mixture explodes if a flame or spark comes in contact with it. This is one of the causes of the explosions which so frequently occur in coal-mines. To prevent these explosions a special lamp was invented by Sir Humphry Davy, which is known as *Davy's safety-lamp* (page 245).

**Substitution-products of the Hydrocarbons.**—Marsh-gas and other hydrocarbons undergo change when treated with chlorine and bromine. The change consists in the substitution of one or more atoms of chlorine or of bromine for the same number of atoms of hydrogen. In the case of marsh-gas and chlorine the possible changes are represented as below:



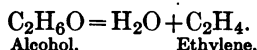
All the products represented are known.

**Chloroform,  $\text{CHCl}_3$ .**—Chloroform can be made as above indicated, but it is made on the large scale by treating alcohol

(page 130) or acetone\* with bleaching-powder. It is a heavy liquid with an ethereal odor and a somewhat sweet taste. It is one of the most valuable anæsthetics.

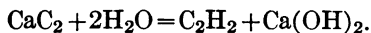
**Iodoform,  $\text{CHI}_3$ .**—This compound, like chloroform, is a substitution-product of marsh-gas. It is made by bringing together alcohol, an alkali, and iodine. It is a solid substance, soluble in alcohol and ether, but insoluble in water. It crystallizes in six-sided yellow plates. It is extensively used as a dressing for wounds in surgery.

**Ethylene, Olefiant Gas,  $\text{C}_2\text{H}_4$ .**— This hydrocarbon is formed by heating a mixture of ordinary alcohol and concentrated sulphuric acid. The reaction is represented thus:



Ethylene is a colorless gas, which can be condensed to a liquid. It burns with a luminous flame. With oxygen it forms an explosive mixture.

**Acetylene,  $\text{C}_2\text{H}_2$ .**—Acetylene is formed when a current of hydrogen is passed between carbon poles, which are incandescent in consequence of the passage of a powerful electric current. In this case carbon and hydrogen combine directly. It is obtained on the large scale by treating calcium carbide (page 390) with water:



It is extensively used for purposes of illumination.

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\* Acetone is a liquid formed when calcium acetate and some other acetates are distilled. Its formula is  $\text{C}_3\text{H}_6\text{O}$ .

## ALCOHOLS.

**Methyl Alcohol, Wood-spirit,  $\text{CH}_4\text{O}$ .**—This is formed in the distillation of wood, and must be separated from the other products which are formed at the same time. It has, when pure, a pleasant odor and taste, and acts upon the animal system very much as ordinary alcohol does, but its internal use is dangerous as it seriously affects the eyes and is known to have caused blindness and even death. It burns without giving light or smoke, and may therefore be used in lamps for heating purposes in place of ordinary alcohol. It is used in the manufacture of varnishes.

**Ethyl Alcohol, Spirits of Wine,  $\text{C}_2\text{H}_6\text{O}$ .**—This well-known substance is formed by the fermentation of grape-sugar, or glucose.

## FERMENTATION.

*Experiment 189.*—(T) Dissolve about 150 grams of commercial grape-sugar in  $1\frac{1}{2}$  litres of water in a flask. Connect the flask by means of a bent glass tube with a cylinder or bottle containing

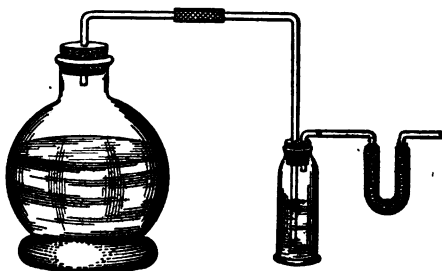


FIG. 55.

clear lime-water. The vessel containing the lime-water must be provided with a cork with two holes. Through one of these passes the tube from the fermentation-flask; through the other



a tube connecting with a vessel containing solid caustic potash, the object of which is to prevent the air from acting upon the lime-water. The arrangement of the apparatus is shown in Fig. 55. Now add to the solution of grape-sugar a little fresh brewers' yeast; close the connections and allow to stand. Soon an evolution of gas will begin, and, as this passes through the lime-water, a precipitate will be formed which can be shown to be calcium carbonate.

**What Change Takes Place in the Sugar?**—If the solution in the flask is examined carefully it will be found to contain alcohol and no sugar. Grape-sugar has the composition expressed by the formula  $C_6H_{12}O_6$ . By fermentation it is decomposed, forming alcohol,  $C_2H_6O$ , and carbon dioxide,  $CO_2$ , thus:



**What Causes the Change?**—It has been found that the change of grape-sugar is caused by small organized bodies which grow in the solution. These bodies are contained in ordinary yeast.

**Germes in the Air.**—When fruit-juices that contain sugar are exposed to the air they undergo fermentation without the addition of yeast. This is due to the fact that the germes or seeds of the bodies that cause fermentation are everywhere floating in the air. Hence when a liquid in which these seeds can grow is exposed to the air, the bodies are formed and fermentation takes place.

**Different Kinds of Fermentation.**—The fermentation which yields alcohol is only one of many kinds. Among the others are: (1) *lactic-acid fermentation*, which takes place in the souring of milk; and (2) *acetic-acid fermentation*, which

causes the transformation of alcohol into acetic acid. The latter ferment is contained in "mother of vinegar."

**Distillation of Fermented Liquids.**—In order to get the alcohol from liquids which have undergone fermentation they must be distilled. For this purpose very perfect forms of stills have been devised, so that the alcohol is obtained from them nearly free from other substances. Usually it contains impurities known as *fusel-oil*.

**Properties of Alcohol.**—Pure ethyl alcohol has a peculiar pleasant odor. It remains liquid at very low temperatures, but has been converted into a solid at a temperature of  $-130.5^{\circ}$ . It burns with a flame which does not deposit soot, and was hence formerly much used in laboratories for heating purposes, and is still used where gas cannot be obtained. Its effects upon the human system are well known. It intoxicates when taken in dilute form, while in large doses it is poisonous. It lowers the temperature of the body when taken internally, although it causes a sensation of warmth.

**Uses of Alcohol.**—Alcohol is the principal solvent for organic substances. It is hence extensively used in the arts, as in the manufacture of varnishes, perfumes, and tinctures of drugs. Most beverages in use owe their intoxicating power to the presence of alcohol. The milder forms of beer contain from 2 to 3 per cent; light wines about 8 per cent; while whiskey, brandy, etc., sometimes contain as much as 60 to 75 per cent.

**Glycerin,  $C_3H_8O_3$ .**—Glycerin is an alcohol which occurs very widely distributed in combination in fats. The rela-

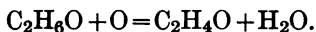
tion it bears to the fats will be explained when the acids which enter into the fats are taken up. It is obtained from the fats by boiling them with an alkali like caustic soda or caustic potash, or by heating with steam.

**Properties.**—Glycerin is a thick, colorless liquid with a sweetish taste. It attracts moisture from the air, and is hence used to keep surfaces moist.

## ALDEHYDES.

**Formic Aldehyde, Formal,  $\text{CH}_2\text{O}$ .**—This compound is prepared by passing the vapor of methyl alcohol together with air over a heated platinum or copper spiral. It is manufactured on the large scale, and comes into the market in solution under the name *formalin*. It is used as a preservative and disinfectant.

**Acetic Aldehyde, Ordinary Aldehyde,  $\text{C}_2\text{H}_4\text{O}$ .**—This compound is formed by oxidizing ordinary alcohol, the change being represented by this equation:

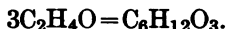


## FORMATION OF ALDEHYDE.

*Experiment 190.*—In a small flask put a few pieces of potassium bichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ , and pour upon it a few cubic centimetres of moderately concentrated sulphuric acid. To this mixture add slowly a few cubic centimetres of ordinary alcohol. Notice the odor.

Aldehyde is a volatile liquid with a characteristic penetrating odor. When left to itself, and especially when treated with a number of other things, it is converted into another substance of the same composition. This is called *paraldehyde*. A determination of the molecular weight of

this substance by the method of Avogadro has shown that it must be represented by the formula  $C_6H_{12}O_3$ . The change from aldehyde to paraldehyde must, therefore, be represented thus:



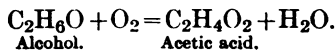
Paraldehyde is used in medicine.

**Chloral**,  $C_2Cl_3HO$ , is a compound formed by the action of chlorine on alcohol. It is related to aldehyde, as chloroform is related to marsh-gas, that is to say, it is a trichlorine substitution-product. It is a colorless liquid. With water it forms a crystallized compound, *chloral hydrate*,  $C_2Cl_3HO + H_2O$ , which is easily soluble in water and crystallizes from the solution in colorless prisms. Taken internally in doses of from 1.5 to 5 grams, it produces sleep. In larger doses it acts as an anæsthetic.

#### ACIDS.

**Formic Acid**,  $CH_2O_2$ .—This acid occurs in nature in red ants, in stinging-nettles, in the shoots of some of the varieties of pine, and elsewhere. It is a colorless liquid. Dropped on the skin, it causes pain and produces blisters.

**Acetic Acid**,  $C_2H_4O_2$ .—This is the acid contained in vinegar, and the value of vinegar is due to its presence. It is formed from alcoholic liquids by exposing them to the air, in consequence of the presence of a microscopic organism which is contained in what is commonly known as "mother of vinegar." The formation of acetic acid from alcohol is due to the action of oxygen as represented in the equation



But oxygen alone does not effect the change. When the ferment is present the oxidation takes place. Acetic acid is also obtained by distilling wood. Hence the names *pyro-ligneous acid* and *wood-vinegar*.

**Properties.**—Acetic acid is a clear, colorless liquid. It has a very penetrating, pleasant odor, and a sharp taste. The pure substance acts upon the skin like formic acid, causing pain and raising blisters.

**Uses.**—Acetic acid is extensively used, chiefly in the dilute form known as vinegar. It is used in calico-printing in the form of iron and aluminium salts. With iron it gives hydrogen, which is needed in the manufacture of certain compounds used in making dyes.

**Salts of Acetic Acid.**—The best-known salts of acetic acid are *lead acetate*,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ , commonly called *sugar of lead*; and *copper acetate*,  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ , a variety of which is known as *verdigris*.

**Fatty Acids.**—Formic and acetic acids are the first members of an *homologous series* (see page 451). Some of the more important members are named in the following table:

Formic acid	.....	$\text{CH}_2\text{O}_2$ .
Acetic "	.....	$\text{C}_2\text{H}_4\text{O}_2$ .
Propionic "	.....	$\text{C}_3\text{H}_6\text{O}_2$ .
Butyric "	.....	$\text{C}_4\text{H}_8\text{O}_2$ .
Palmitic "	.....	$\text{C}_{16}\text{H}_{32}\text{O}_2$ .
Stearic "	.....	$\text{C}_{18}\text{H}_{36}\text{O}_2$ .

They are called *fatty acids* for the reason that many of them have the consistency of fats.

**Butyric acid**,  $C_4H_8O_2$ , is of special interest because it is obtained from butter by boiling with caustic potash. It occurs also in many other fats. There is a *butyric-acid ferment* contained in putrid cheese which has the power of converting sugar into butyric acid.

**Palmitic acid**,  $C_{16}H_{32}O_2$ , is obtained from many fats, but palm-oil is especially rich in it.

**Stearic acid**,  $C_{18}H_{36}O_2$ , is the acid contained in the fat known as *stearin*. The so-called "*stearin* candles" are made of a mixture of palmitic and stearic acids.

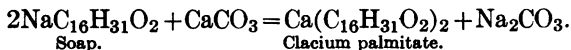
**Soaps.**—Soaps are the alkali salts of the acids contained in fats, especially of palmitic and stearic acids. Fats are compounds of these acids with glycerin. When the fats are boiled with an alkali, as caustic soda, the corresponding salts of the acids are formed, while the glycerin is set free. The palmitate and stearate of potassium and sodium are the soaps.

#### SOAP-MAKING.

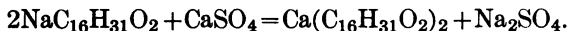
*Experiment 191.*—Put a piece of lard the size of a grape in an evaporating-dish. Add a few (4 or 5) cubic centimetres of alcohol and 10 drops of a 50 per cent solution of sodium hydroxide. Heat very gently and stir the contents of the dish. Boil until the odor of alcohol has disappeared. Evaporate to dryness. Is the residue soluble in water? If not add a little more alcohol and sodium hydroxide and repeat the boiling. The fat should be saponified and the product should be a soap.

**Use of Soap.**—The cleansing power of soap depends upon the fact that it removes the oily film on the surface of the skin and thus facilitates the removal of the foreign substances commonly known as dirt.

**Action of Soap on Hard Waters.**—As has been explained, a hard water is one that contains calcium or magnesium salts in solution (see pages 234, 396). *Temporary hardness* is that which is caused by calcium carbonate held in solution in the water by carbon dioxide. *Permanent hardness* is caused by calcium sulphate or magnesium salts. The calcium and magnesium salts of palmitic and stearic acids are insoluble in water. Therefore, when soap is added to a hard water these insoluble salts are precipitated and give the water a hard feeling. In attempting to wash the hands with soap in a hard water they become covered with a thin layer of the insoluble salts which prevents them from rubbing freely over each other and makes them feel sticky. Before the soap can serve its purpose all the calcium salt must be precipitated. The action in the case of temporary hardness is represented by the equation



In the case of permanent hardness it is represented by the equation



#### ACTION OF SOAP ON HARD WATER (TEMPORARY HARDNESS).

*Experiment 192.*—Make some hard water by passing carbon dioxide through dilute lime-water until the precipitate first formed is dissolved again. Filter. Make a solution of soap by shaking a few shavings of soap with water. Filter. Add the solution of soap to the hard water. Is a precipitate formed? Rub a piece of soap between the hands wet with the hard water,

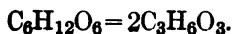
## ACTION OF SOAP ON HARD WATER (PERMANENT HARDNESS).

*Experiment 193.*—Make some hard water by shaking a litre of water with a little powdered gypsum. Perform with it the same experiments as those performed with the water containing calcium carbonate.

**Relations of the Soap Industry to other Industries.**—A great chemist and philosopher has said that the quantity of soap used in a country is a measure of the civilization of that country. Certain it is that soap is only used by civilized people, and that by them it is used in enormous quantities. In many farm-houses a primitive method for the manufacture of soap is practised, consisting in treating refuse fats with the lye extracted from wood-ashes. A soft soapy mass is thus obtained known as “soft-soap.” Fats form the starting-point in the manufacture of all soap. These are generally treated for the purpose with caustic soda.

**Oxalic Acid,  $C_2H_2O_4$ .**—This acid occurs very widely distributed in nature, as in the *sorrels*, which owe their acid taste to the presence of acid potassium oxalate,  $KC_2HO_4$ ; and as the ammonium salt in guano. It is probably one of the first substances formed from carbon dioxide in the plant. It is manufactured by heating wood shavings or sawdust with caustic soda and caustic potash. Oxalic acid is an active poison. It is used in calico-printing, and in cleaning brass and copper surfaces.

**Lactic Acid,  $C_3H_6O_3$ .**—Lactic acid is made by the fermentation of sugar by means of the *lactic-acid ferment*. The reaction effected by the ferment is represented by the equation





**Malic Acid,  $C_4H_6O_5$ .**—This acid is widely distributed in the vegetable kingdom, as in apples, cherries, etc.

**Tartaric Acid,  $C_4H_6O_6$ .**—Tartaric acid occurs widely distributed in fruits, sometimes uncombined, sometimes in the form of the potassium or calcium salt; as, for example, in grapes, berries of the mountain-ash, potatoes, cucumbers, etc., etc. It is prepared from "cream of tartar." This is acid potassium tartrate, which is formed when grape-juice ferments.

**Citric Acid,  $C_6H_8O_7$ .**—Citric acid, like malic and tartaric acids, is very widely distributed in nature in many varieties of fruit, especially in lemons. It is also found in currants, whortleberries, raspberries, gooseberries, etc., etc. It is prepared from lemon-juice: 100 parts of lemon yield  $5\frac{1}{2}$  parts of the acid. It is a solid, crystallized substance, soluble in water. It is frequently used for the purpose of making lemonade without lemons, and there is no objection to its use for this purpose.

#### ETHERS.

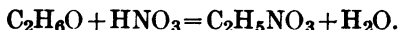
**Ether,  $C_4H_{10}O$ .**—Ordinary ether is the best-known representative of the class of compounds called *ethers*. It is formed from ordinary alcohol by treating it with sulphuric acid and distilling. The result of the action which takes place is represented by the equation



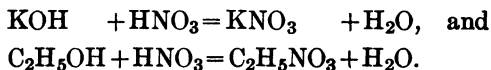
Ether is a liquid which boils at a low temperature and takes fire and burns readily. Inhaled it produces insensibility to pain. It is therefore called an *anæsthetic*.

## ETHEREAL SALTS.

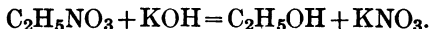
**Action of Acids upon Alcohols.**—When an acid acts upon an alcohol it is neutralized, though not as readily as when it acts upon a base. The product is a substance which resembles a salt and is called an ethereal salt. Thus when nitric acid acts upon alcohol this reaction takes place:



The product  $\text{C}_2\text{H}_5\text{NO}_3$ , called ethyl nitrate, is an ethereal salt. The alcohol acts as if it were a substance like caustic potash and made up thus,  $\text{C}_2\text{H}_5\text{OH}$ . The resemblance between its action and that of caustic potash is shown by the equations:



**Saponification.**—When an ethereal salt is boiled with a caustic alkali it is decomposed, the products being an alcohol and an alkali salt. Thus when ethyl nitrate is boiled with caustic potash, potassium nitrate and alcohol are formed:



This process is called *saponification*, because the most important example is furnished by soap-making.

**Fats.**—The fats are ethereal salts in the formation of which glycerin, as the alcohol, and three acids take part. The three acids are palmitic and stearic acids, already mentioned, and *oleic acid*,  $\text{C}_{18}\text{H}_{34}\text{O}_2$ . Although the composition of these substances is comparatively complex, the

way they act upon one another is simple, and is the same as the action of nitric acid upon alcohol in forming ethyl nitrate. The fats, then, are the palmitate, stearate, and oleate of *glyceryl*, which bears to glycerin very much the same relation that ethyl,  $C_2H_5$ , bears to alcohol. When a fat is boiled with caustic soda, glycerin and the sodium salts of the acids contained in the fat are formed.

**Butter** consists of ethereal salts of glycerin and several fatty acids, among which are palmitic, stearic, and butyric. *Oleomargarin* is an artificial butter made from other fats than that of milk.

**Ethereal Salts as Essences.**—The ethereal salts generally have pleasant odors, and it is to their presence that many fruits owe their flavors. Some of the compounds are now made artificially and used instead of the fruit-extracts. Thus the *ethyl salt of butyric acid* is used under the name of *essence of pineapples*, and the *amyl salt of valeric acid* under the name of *essence of apples*.

**Nitroglycerin.**—Among the more important ethereal salts of glycerin are the *nitrates*. Two of these are known,

*viz.*, the mono-nitrate,  $C_3H_5 \begin{cases} O.NO_2 \\ OH \\ OH \end{cases}$ , and the *trinitrate*,

$C_3H_5(O.NO_2)_3$ , the latter being the chief constituent of *nitroglycerin*. Nitroglycerin is prepared by treating glycerin with a mixture of concentrated sulphuric and nitric acids. It is a pale-yellow oil which is insoluble in water. At  $-20^\circ$  it crystallizes in needles. It explodes very violently by concussion. It may be burned in an open vessel, but if

heated above  $250^{\circ}$  it explodes. *Dynamite* is infusorial earth \* impregnated with nitroglycerin. Nitroglycerin is the active constituent of a number of explosives.

#### RELATIONS BETWEEN THE COMPOUNDS CONSIDERED.

**Comparison of the Formulas.**—On comparing the formulas of the hydrocarbons of the marsh-gas series (see page 502) with those of the simplest alcohols and the fatty acids, it will be seen that these compounds are all related in a simple way. Below are lists of a few of the hydrocarbons, alcohols, and acids;

Hydrocarbons.	Alcohols.	Acids.
$\text{CH}_4$	$\text{CH}_4\text{O}$	$\text{CH}_2\text{O}_2$
$\text{C}_2\text{H}_6$	$\text{C}_2\text{H}_6\text{O}$	$\text{C}_2\text{H}_4\text{O}_2$
$\text{C}_3\text{H}_8$	$\text{C}_3\text{H}_8\text{O}$	$\text{C}_3\text{H}_6\text{O}_2$
$\text{C}_4\text{H}_{10}$ , etc.	$\text{C}_4\text{H}_{10}\text{O}$ , etc.	$\text{C}_4\text{H}_8\text{O}_2$ , etc.

Each of these series is an homologous series.

**Alcohols.**—Alcohols have been shown to be derived from the hydrocarbons by the replacement of one or more hydrogen atoms by oxygen and hydrogen,  $\text{OH}$ , called *hydroxyl*, or from water by replacing one of the hydrogen atoms of the water by a group composed of carbon and hydrogen. An alcohol, then, is a hydroxide, just as a metallic base is; only, instead of consisting of a metal in combination with hydroxyl, it consists of a compound of carbon and hydrogen in combination with hydroxyl. Thus:

Metallic Bases.	Alcohols.
$\text{K}(\text{OH})$	$\text{CH}_3(\text{OH})$
$\text{Na}(\text{OH})$	$\text{C}_2\text{H}_5(\text{OH})$

\* That is to say, earth made up of the microscopic flinty shells which constitute the fossil remains of certain minute and simple plants.

**More Complex Alcohols.**—Just as lime is a more complex base than caustic potash, as shown by the formulas  $\text{KOH}$  and  $\text{CaO}_2\text{H}_2$  or  $\text{Ca}(\text{OH})_2$ , so there are more complex alcohols than ordinary alcohol. A good example is furnished by glycerin,  $\text{C}_3\text{H}_8\text{O}_3$ , which has been shown to be a hydroxide corresponding to aluminium hydroxide,  $\text{Al}(\text{OH})_3$ , a fact which is represented by the formula  $\text{C}_3\text{H}_5(\text{OH})_3$ . It may be called glyceryl hydroxide, the complex  $\text{C}_3\text{H}_5$  being known as glyceryl.

**Radicals or Residues.**—The compounds of hydrogen and carbon contained in the alcohols are called *radicals* or *residues*. We may say that an alcohol is water in which half of the hydrogen has been displaced by a radical.

$\text{HOH}$   
Water.

$\text{C}_2\text{H}_5\text{OH}$   
Ordinary alcohol.

$\text{HOH}$   
 $\text{HOH}$   
 $\text{HOH}$   
Water.

$\text{C}_3\text{H}_5 \begin{cases} \text{OH} \\ \text{OH} \\ \text{OH} \end{cases} = \text{C}_3\text{H}_8\text{O}_3$ .  
Glycerin.

**Acids.**—Just as the alcohols have been shown to be derived from water, so the organic acids have been shown to be derived from carbonic acid. The carbonates are derived from an acid of the formula  $\text{H}_2\text{CO}_3$ , or  $\text{CO} \begin{Bmatrix} \text{OH} \\ \text{OH} \end{Bmatrix}$ . If, in this acid, a hydroxyl is replaced by a radical, as, for example, by ethyl,  $\text{C}_2\text{H}_5$ , a substance of the formula  $\text{CO} \begin{Bmatrix} \text{C}_2\text{H}_5 \\ \text{OH} \end{Bmatrix}$  or  $\text{C}_3\text{H}_6\text{O}_2$  is the result. If methyl,  $\text{CH}_3$ , is introduced in place of ethyl, the product is  $\text{CO} \begin{Bmatrix} \text{CH}_3 \\ \text{OH} \end{Bmatrix}$  or  $\text{C}_2\text{H}_4\text{O}_2$ , which is acetic acid. In a similar way all the organic acids are derived from carbonic acid.

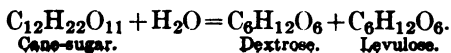
## CHAPTER XXXI.

### OTHER COMPOUNDS OF CARBON.

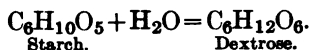
**The Carbohydrates.**—The carbohydrates form an important group of carbon compounds which include the most abundant substances found in the vegetable kingdom. Besides carbon, most of them contain hydrogen and oxygen in the proportions to form water. Hence they have been called carbohydrates. The chief compounds included under this head are *grape-sugar or glucose, cane-sugar, starch, cellulose, gum, and dextrin.*

**Grape-sugar, Glucose, Dextrose,  $C_6H_{12}O_6$ .**—Dextrose occurs very widely distributed in plants, particularly in sweet fruits. It is found also in honey and, further, in the liver and the blood.

**Formation of Dextrose.**—Dextrose or glucose is formed from several of the carbohydrates by boiling with dilute mineral acids, or by the action of ferments. Its formation from cane-sugar takes place according to this equation, equal quantities of dextrose and levulose being formed:



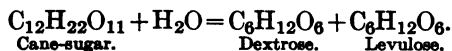
Its formation from starch is represented by this equation:



**Manufacture of Dextrose or Glucose.**—Dextrose is prepared on the large scale from corn-starch in the United States, and from potato-starch in Germany. The change is usually effected by boiling with dilute sulphuric acid. The acid is afterwards removed by treating with chalk, and filtering. [Explain how this removes the acid.] The filtered solutions are evaporated either to a syrupy consistency, and sent into the market under the names "glucose," "mixing-syrup," etc.; or to dryness, the solid product being known as "grape-sugar."

**Properties.**—Dextrose crystallizes from concentrated solutions, and as seen in commercial "granulated grape-sugar" looks very much like granulated cane-sugar. It is sweet, but not as sweet as cane-sugar. It is estimated that the sweetness of dextrose is to that of cane-sugar as 3 : 5. Under the influence of yeast it ferments, yielding mainly alcohol and carbon dioxide. Putrid cheese transforms it into lactic acid, and then into butyric acid.

**Levulose, Fruit-sugar,  $\text{C}_6\text{H}_{12}\text{O}_6$ .**—This form of sugar occurs with dextrose in fruits; and is formed by the action of dilute acids or ferments on cane-sugar, which breaks up according to the equation



As cane-sugar is found in unripe fruits, it is probable that the change represented in the equation takes place during the process of ripening.

**Cane-sugar,**  $C_{12}H_{22}O_{11}$ .—This well-known variety of sugar occurs very widely distributed in nature—in sugar-cane, sorghum, the Java palm, the sugar-maple, beets, madder-root, coffee, walnuts, hazel-nuts, sweet and bitter almonds; in the blossoms of many plants, etc.

**Sugar-refining.**—Sugar is obtained mainly from the sugar-cane and beets. In either case the processes of extraction and refining are largely mechanical. When sugar-cane is used, this is macerated with water to dissolve the sugar. Thus a dark-colored solution is obtained. This is evaporated, and then passed through filters of bone-black by which the color is removed. The clear solution is then evaporated in open vessels to some extent; and, finally, in large closed vessels called “vacuum-pans,” from which the air is partly exhausted, so that the boiling takes place at a lower temperature than is required under the ordinary pressure of the atmosphere. The mixture of crystals and mother-liquors obtained from the “vacuum-pans” is freed from the liquid by being brought into the “centrifugals.” These are funnel-shaped sieves which are revolved rapidly, the liquid being thus thrown by centrifugal force through the openings of the sieve, while the crystals remain behind and are thus nearly dried. The final drying is effected by placing the crystals in a warm room.

**Molasses.**—The mother-liquors obtained from the “centrifugals” are further evaporated, and yield lower grades of sugar; and, finally, a syrup is obtained which does not crystallize. This is *molasses*.

**Properties of Sugar.**—Sugar crystallizes from water in large well-formed prisms. When heated to  $210^{\circ}$  to  $220^{\circ}$ ,



it loses water, and is converted into a substance called *caramel*, which is colored more or less brown. When boiled with dilute acids, cane-sugar is split into equal parts of dextrose and levulose. The mixture of the two is called *invert-sugar*. Yeast gradually transforms cane-sugar into dextrose and levulose, and these then undergo fermentation. Cane-sugar does not ferment.

**Sugar of Milk, Lactose,  $C_{12}H_{22}O_{11} + H_2O$ .**—This sugar occurs in the milk of all mammals. It is obtained in the manufacture of cheese. Cow's milk consists of water, casein, butter, sugar of milk, and a little inorganic material, in about the following proportions:

Water.....	87 per cent
Casein.....	4 " "
Butter.....	3½ " "
Sugar of milk.....	4½ " "
Mineral matter.....	½ " "
	<hr/>
	100 " "

Cheese is made by adding rennet to milk, which causes the separation of the casein. The sugar of milk remains in solution, is separated by evaporation, and purified by recrystallization. It has a slightly sweet taste, and is much less soluble in water than cane-sugar.

**Souring of Milk.**—Sugar of milk ferments under certain circumstances, and is transformed mostly into lactic acid. The souring of milk is a result of this fermentation. The lactic acid formed coagulates the casein; hence the thickening.

**Cellulose,  $C_6H_{10}O_5$ .**—Cellulose forms, as it were, the groundwork of all vegetable tissues. It presents different appear-

ances and different properties, according to the source from which it is obtained; but these differences are due to substances with which the cellulose is mixed; and when they are removed, the cellulose left behind is the same thing, no matter what its source may have been. The coarse wood of trees and the tender shoots of the most delicate plants consist essentially of cellulose. Cotton, wool, hemp, and flax consist almost wholly of cellulose.

**Properties.**—Cellulose does not crystallize, and is insoluble in all ordinary solvents. It dissolves in concentrated sulphuric acid. If the solution is diluted and boiled, the cellulose is converted into dextrin and dextrose. It will thus be seen that rags, paper, and wood, all of which consist largely of cellulose, might be used for the preparation of dextrose or glucose, and consequently of alcohol.

**Gun-cotton, Pyroxylin, Nitrocellulose.**—Cellulose has some of the properties of alcohols; among them the power to form ethereal salts with acids. Thus, when treated with nitric acid it forms several nitrates, just as glycerin forms the nitrate known as nitroglycerin (page 517). The nitrates are explosive, and are used for blasting under the name *gun-cotton*.

**Collodion.**—A solution of gun-cotton in a mixture of ether and alcohol is known as *collodion solution*, which is much used in photography. When poured upon any surface, such as glass, the ether and alcohol rapidly evaporate, leaving a thin coating of gun-cotton.

**Celluloid.**—Celluloid is an intimate mixture of gun-cotton and camphor. As it is plastic at a slightly elevated tem-

perature, it can easily be moulded into any desired shape. When cooled it hardens.

**Paper.**—Paper in its many forms consists mainly of cellulose. The essential features in the manufacture of paper are, first, the disintegration of the substances used. This is effected partly mechanically and partly by boiling with caustic soda. Then the resulting mass is converted into pulp by means of knives placed on rollers. The pulp, with the necessary quantity of water, is then passed between rollers. Rags of cotton or linen are chiefly used in the manufacture of paper; wood and straw are also used.

**Starch,  $C_6H_{12}O_5$ .**—Starch is found everywhere in the vegetable kingdom in large quantity, particularly in all kinds of grain, as maize, wheat, etc.; in tubers, as the potato, arrowroot, etc.; in fruits, as chestnuts, acorns, etc.

**Manufacture of Starch.**—In the United States starch is manufactured mainly from maize; in Europe, from potatoes. The processes employed are mostly mechanical. The maize is first treated with warm water; the softened grain is then ground between stones, a stream of water running constantly into the mill. The thin paste which is carried away is brought upon sieves of silk bolting-cloth, which are kept in constant motion. The starch passes through with the water as a milky fluid. This is allowed to settle when the water is drawn off. The starch is next treated with water containing a little alkali, the object of which is to dissolve gluten, oil, etc. The mixture is now brought into shallow, long wooden runs, where the starch is deposited, the alkaline water running off. Finally, the

starch is washed with water, and dried at a low temperature.

**Properties.**—Starch in its usual condition is insoluble in water. If ground with cold water it is partly dissolved. If heated with water the membranes of the cells of which the starch is composed are broken, and the contents form a partial solution. On cooling, it forms a transparent jelly called *starch-paste*. By dilute acids and ferments starch is converted into dextrin, maltose, and dextrose.

**Flour.**—Wheat flour, which may serve as an example of flour in general, contains water, starch with a little sugar and gum, *gluten*, and a small quantity of mineral matter. The finest flour contains about 10 per cent of gluten and 70 per cent of starch. Gluten is a substance that in many respects resembles the white of eggs, or egg-albumin.

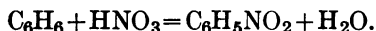
**Bread-making.**—The chemical changes which take place in bread-making are of special interest. Bread is made by mixing the flour with water and a little yeast. The dough thus prepared is put in a warm place for a time, when it rises. The rising is a result of fermentation caused by the yeast. A part of the starch contained in the flour is converted into sugar, and this is then converted into alcohol and carbon dioxide by fermentation. The alcohol passes off for the most part, and the carbon dioxide in striving to escape from the thick gummy dough fills the mass with bubbles of gas, making it light and porous. When the loaf is put into the oven the gases contained in it expand, making it still lighter; then the fermentation is checked by the heat and no further chemical change takes place

except on the surface, where the substances are partly decomposed and converted into a dark-colored product, the crust.

A FEW COMPOUNDS FROM COAL-TAR.

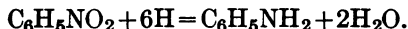
**Aromatic Compounds.**—The fact that benzene,  $C_6H_6$ , toluene,  $C_7H_8$ , and other hydrocarbons are obtained from coal-tar has already been mentioned (page 499). These hydrocarbons are the starting-points for the preparation of a very large number of compounds of carbon which are commonly called the "aromatic compounds," as many of them have a pleasant aromatic odor.

**Nitrobenzene,  $C_6H_5NO_2$ .**—This substance is formed by treating benzene with nitric acid:



It is a yellow liquid with a pleasant odor like that of the oil of bitter almonds. It is much used under the name *artificial oil of bitter almonds*.

**Aniline,  $C_6H_5NH_2$ .**—When nitrobenzene is treated with a solution from which hydrogen is given off the oxygen is extracted and replaced by hydrogen:



The product is the substance known as aniline. It is a colorless liquid. When it together with a similar substance, known as toluidine, is treated with mercuric chloride,  $HgCl_2$ , or arsenic acid it is converted into the dye *magenta*, which is the substance from which most of the aniline dyes are prepared.

**Aniline Dyes.**—Of these a large number are known. They are all derivatives of rosaniline, of which magenta is a salt. A great many different colors of aniline dyes are made, some of them of great beauty.

**Phenol, Carboic Acid,  $C_6H_6O$ .**—This familiar substance is contained in coal-tar, and is extracted from it by treating with caustic soda in which the carboic acid dissolves. When pure it crystallizes in beautiful colorless rhombic needles. It has a peculiar, penetrating odor, and is poisonous. It is much used as a disinfectant.

**Trinitrophenol, Picric Acid,  $C_6H_3O(NO_2)_3$ ,** is made by the action of nitric acid on phenol. Picric acid is a lemon-yellow, crystalline substance, used as a yellow dye and as an explosive.

**Explosives.**—All explosives contain nitrogen, and their explosiveness depends on the instability of compounds of nitrogen and oxygen and on the great stability of molecular nitrogen, which last—with other substances—is the product of all explosives.

Explosives are of two types, *instantaneous* and *progressive*. Suitable dilution of an instantaneous explosive renders it less violent.

The most important instantaneous explosives are nitroglycerin, dynamite in its many forms of dilution, and blasting gelatin, which is the most violent explosive known. It is made by mixing about 95 parts of nitroglycerin with 5 parts of gun-cotton; it is a gelatinous mass.

The most violent explosions are initiated by the explosion of a cap of mercury fulminate. The *character* of an explosion depends on the character of the initial shock.

*Progressive explosives* are common black gunpowder, nitro-cellulose powders, and picric acid powders. *Gunpowder* is now mostly replaced for blasting purposes by dynamite and blasting gelatin, and for cannon and small-arm purposes by the powders just mentioned.

*Nitro-cellulose powders.*—Gun-cotton is “colloided” by dissolving it in a mixture of alcohol and ether, and evaporating the solution; a tough amorphous solid or colloid remains. This in granulated form is a “*smokeless powder*.”

As nitro-cellulose has too little oxygen to oxidize the carbon completely, either nitro-glycerin or metallic nitrates are generally added to supply the oxygen, in making smokeless powders.

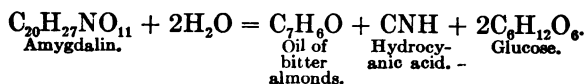
*Cordite*, the English smokeless powder, is a mixture of colloided gun-cotton with nitroglycerin and vaseline. The smokeless powder used for small-arms by the army of the United States contains colloided gun-cotton and potassium nitrate or barium nitrate.

Picric acid and ammonium picrate are also utilized as smokeless powders. The French mellinite and the English lyddite\* are both chiefly picric acid.

**Oil of Bitter Almonds, Benzoic Aldehyde,** }  $C_7H_6O$ .—This substance occurs in combination with amygdalin, which is found in bitter almonds, laurel-leaves, cherry-kernels, etc. Amygdalin belongs to the class of compounds known as *glucosides*, which break up into glucose and other substances. Amygdalin itself, under

\* In the last war in South Africa after some of the battles the hands and faces of the combatants were seen to be colored yellow. This must have been due to the picric acid contained in the lyddite used by the English.

the influence of *emulsin*, which occurs with it in the plants, breaks up into oil of bitter almonds, hydrocyanic acid, and dextrose:



It is prepared from bitter almonds, which yield about 1.5 to 2 per cent. It is a liquid with a pleasant odor. It is made artificially from coal-tar, and was at one time used in the artificial preparation of indigo.

**Benzoic Acid,  $\text{C}_7\text{H}_6\text{O}_2$ .**—Benzoic acid occurs in gum benzoin and in the balsams of Peru and Tolu, and is made artificially from coal-tar by oxidizing toluene,\*  $\text{C}_7\text{H}_8$ .

**Balsams and Odoriferous Resins.**—The balsams of Peru and Tolu are thick fragrant fluids which are obtained from certain trees in South America and elsewhere by cutting the bark. Benzoin is a similar substance. These as well as myrrh, frankincense, and other substances of the kind are used for their odors. The odors are intensified when the substances are heated. They are largely used as *incense*.

**Gallic Acid,  $\text{C}_7\text{H}_6\text{O}_5$ .**—Gallic acid occurs in sumach, in Chinese tea, and many other plants. It is formed by boiling tannin or tannic acid with sulphuric acid. It is prepared from gall-nuts by fermentation of the tannin contained in them. It is closely related to tannin or tannic acid.

\* The name toluene comes from the fact that this hydrocarbon was first obtained from the balsam of Tolu.



**Tannic Acid, Tannin,**  $C_{14}H_{10}O_3$ .—This substance occurs in gall-nuts, from which it is extracted in large quantities. It is soluble in water. Its solution gives a dark blue-black color with iron salts. Tannin is used extensively in medicine, in dyeing, in the manufacture of leather and of ink.

#### ACTION OF TANNIN ON FERROUS SULPHATE.

*Experiment 194.*—Boil 10 grams of powdered gall-nuts with 60 cc. of water, adding water from time to time. A solution of tannin is thus obtained. Filter after standing. In a test-tube add to some of this solution a few drops of a solution of copperas (ferrous sulphate). A colored precipitate is formed which gradually changes to black.

**Tanning.**—The process of tanning consists in treating hides, from which the hair has been removed, with an infusion of hemlock or oak bark, or of sumach-leaves, in which there is tannic acid. The acid combines with certain parts of the hides, forming insoluble compounds which remain in the pores, converting the hides into leather.

**Indigo.**—In several plants which grow in the East and West Indies, in South America, Egypt, and other warm countries, there occurs a substance called *indican* which, when treated with dilute mineral acids or certain ferments, breaks up into indigo-blue and a substance resembling glucose. Commerical indigo contains as its principal ingredient indigo-blue. Indigo-blue is now manufactured by artificial methods on the large scale.

**Naphthalene,**  $C_{10}H_8$ .—This hydrocarbon is contained in coal-tar in large quantity. It is a beautiful white crystallized substance much used in the preparation of dyes and for protecting woollen fabrics from moth.

**Anthracene,  $C_{14}H_{10}$ .**—Anthracene like naphthalene is obtained from coal-tar. Its chief use is in the preparation of artificial alizarin.

**Alizarin,  $C_{14}H_8O_4$ .**—Alizarin is the well-known dye obtained from madder-root. For some years it has been made artificially from anthracene, and the cultivation of madder has been given up. Madder-root was used for dyeing "Turkey-red." Artificial alizarin is exclusively used for this purpose at present.

**Glucosides.**—Glucosides are substances that occur in nature in the vegetable kingdom. They break down under the influence of ferments and dilute acids into sugar and other compounds. Amygdalin has already been mentioned. This breaks down into oil of bitter almonds and dextrose. Indican, which yields indigo and dextrose, is another example.

**Myronic acid,** another glucoside, is found in the form of the potassium salt in black mustard-seed. When treated with myrosin, which is contained in the aqueous extract of white mustard-seed, potassium myronate is converted into dextrose and oil of mustard.

**Alkaloids.**—These compounds occur in plants, and are frequently those parts of the plants which are most active when taken into the animal body. They are hence sometimes called the *active principles* of plants. Many of these substances are used in medicine. They all contain nitrogen and in some respects resemble ammonia. Only a few of the more important alkaloids need be mentioned here.

**Quinine.**—This valuable alkaloid is obtained from the

outer bark of certain trees which grow in Peru. The bark is known as Peruvian bark.

**Cocaine** is found in coca-leaves. Its hydrochloric-acid salt has come into prominence in medicine, owing to the fact that a small quantity of its solution placed upon the eye or the gums or injected beneath the skin causes insensibility to pain.

**Nicotine** occurs in tobacco-leaves in combination with malic acid.

**Morphine** and **narcotine** are the principal alkaloids found in *opium*, which is the evaporated sap that flows from incisions in the capsules of the white poppy before they are ripe.

## CHAPTER XXXII.

### QUALITATIVE ANALYSIS.

**General.**—In order to analyze substances chemists make use of reactions such as have been studied in the earlier parts of this book. To learn to analyze complicated substances, long practice and careful study of a great many facts are necessary. But simple substances can be analyzed by the aid of such facts as have already been studied. It has been seen, for example, that certain chlorides are insoluble in water; that certain sulphides are insoluble in dilute hydrochloric acid; and that other sulphides which are soluble in dilute hydrochloric acid are insoluble in neutral or alkaline solutions. Advantage is taken of these and other similar facts to classify substances according to their reactions. A convenient classification for purposes of analysis is the following:

GROUP I. Metals whose chlorides are insoluble or difficultly soluble in water. This group includes: *Silver, lead, and mercury* (as mercurous salt).

GROUP II. Metals not included in Group I, whose sulphides are, however, insoluble in dilute hydrochloric or nitric acid. This group includes: *Copper, mercury* (as mercuric salt), *bismuth, antimony, arsenic, and tin.*

GROUP III. Metals not included in Groups I and II, whose sulphides are, however, precipitated by ammonium sulphide and ammonia. This group includes: *Aluminium, chromium, nickel, cobalt, iron, zinc, and manganese.*

GROUP IV. Metals not included in Groups I, II, and III, but which are precipitated by ammonium carbonate, ammonia, and ammonium chloride. This group includes: *Barium, strontium, and calcium.*

GROUP V. Metals not included in Groups I, II, III, and IV, but which are precipitated by disodium phosphate  $\text{HNa}_2\text{PO}_4$ , ammonia, and ammonium chloride. This group includes: *Magnesium.*

GROUP VI. Metals not included in Groups I, II, III, IV, and V. This group includes: *Sodium, potassium, and ammonium.*

1. Now, suppose you have a substance given you for analysis. The first thing to do is to get the substance in solution. See whether it dissolves in water. If it does not, try dilute hydrochloric acid. If it does not dissolve in hydrochloric acid, try nitric acid; and if it does not dissolve in nitric acid, try a mixture of nitric and hydrochloric acids. If concentrated acid is used, evaporate to dryness on a water-bath before proceeding further. Then dissolve in water, and add a few drops of hydrochloric acid. If a precipitate is formed, continue to add the acid drop by drop until a precipitate is no longer formed. Filter and wash.

What may this precipitate contain?

2. Pass hydrogen sulphide through the filtrate for some time and let stand. Filter and wash.

If a precipitate is formed, what may it contain?

3. Add ammonia and ammonium sulphide to the filtrate. Filter and wash.

If a precipitate is formed, what may it contain?

4. Add ammonium chloride, ammonia, and ammonium carbonate, to the filtrate. Filter and wash.

If a precipitate is formed, what may it contain?

5. Add disodium phosphate, ammonia, and ammonium chloride to the filtrate. Filter and wash.

If a precipitate is formed, what may it contain?

What may be in the filtrate?

**Examples for Practice.**—Before attempting anything in the way of systematic analysis it will be well to experiment in a more general way, with the object of determining which one of a given list of substances a certain specimen is.

The list below contains the names of the principal substances with which you have thus far had directly to deal in your work. You have handled them and have seen how they act toward different substances. Suppose now that a substance is given you, and you know simply that it is one of those named in the list, how would you go to work to find out which one it is? You have a right to judge by anything in the appearance or in the conduct of the substance. If you reach a conclusion, see whether you are right by further experiments. After your work is finished write out a clear account of what you have done, and state your reasons for the conclusion you have reached.

For example, suppose sodium chloride is given you. You see that it is a white solid. On heating it in a small tube, you see that it does not melt, but it breaks up into smaller pieces with a crackling sound. It is soluble in water. Hy

drochloric acid causes no change when added to a little of the solid. Is it a carbonate? Sulphuric acid causes evolution of a gas. Has this an odor? How does it appear when allowed to escape into the air? Is it nitric acid? Collect some of it in water. How does this solution act on a solution of silver nitrate? By this time you have evidence that you are dealing with a chloride, but you do not yet know which chloride it is. It cannot be ammonium chloride. Why? It may be either potassium or sodium chloride.

Try a small piece in the flame. What color? You now have good reasons for believing that the substance you are dealing with is sodium chloride. To convince yourself, get a small piece of sodium chloride from the bottle known to contain it, and make a series of parallel experiments with this and see whether you get exactly the same results that you got with the specimen you were examining. If not, account for the differences.

By careful work there will be no serious difficulty in determining which one of the substances in the list you are dealing with.

#### List of Substances for Examination.

- |                       |                                  |
|-----------------------|----------------------------------|
| 1. Sugar.             | 10. Tin.                         |
| 2. Mercuric oxide.    | 11. Oxalic acid.                 |
| 3. Calc spar.         | 12. Sodium carbonate.            |
| 4. Marble.            | 13. Ferrous sulphate (Copperas). |
| 5. Copper.            | 14. Roll-sulphur.                |
| 6. Hydrochloric acid. | 15. Iron-filings.                |
| 7. Nitric acid.       | 16. Carbon bisulphide.           |
| 8. Sulphuric acid.    | 17. Lead.                        |
| 9. Zinc.              |                                  |

- |                                |                           |
|--------------------------------|---------------------------|
| 18. Potassium chlorate.        | 26. Ammonium nitrate.     |
| 19. Manganese dioxide.         | 27. Sodium chloride.      |
| 20. Charcoal.                  | 28. Potassium bromide.    |
| 21. Calcium sulphate (Gypsum). | 29. Potassium iodide.     |
| 22. Copper oxide.              | 30. Iron sulphide.        |
| 23. Ammonium chloride.         | 31. Potassium carbonate.  |
| 24. Calcium oxide (Quicklime). | 32. Potassium nitrate.    |
| 25. Sodium nitrate.            | 33. Potassium dichromate. |
|                                | 34. Red lead (Minium).    |
|                                | 35. Lead nitrate.         |

[The instructor will, of course, select the substance and give it to the student without any suggestion as to what it is. After the student has shown that he can tell with certainty which substance he has, some simple mixtures of substances selected from the above list may next be given for examination. Thus charcoal and copper oxide; zinc and tin; mercuric oxide and iron-filings; etc., etc.]

#### STUDY OF GROUP I.

*Experiment 195.*—1. Prepare dilute solutions of silver nitrate,  $\text{AgNO}_3$ , lead nitrate,  $\text{Pb}(\text{NO}_3)_2$ , and mercurous nitrate,  $\text{HgNO}_3$ .

2. Add to a small quantity of each separately in test-tubes a little hydrochloric acid.

What is formed?

3. Heat each tube with contents, and then let cool.

What difference do you observe?

4. After cooling, add a little ammonia to the contents of each tube.

What takes place in each case?

How could you distinguish between silver, lead, and mercury?

5. Mix the solutions of silver nitrate, lead nitrate, and mercurous nitrate, and add a little of the mixture to considerable water in a test-tube. Add hydrochloric acid as long as it causes



the formation of a precipitate. Heat to boiling. Filter rapidly and wash with hot water.

What is in the filtrate, and what is on the filter?

6. Let the filtrate cool.

What evidence have you that there is anything present in it?

7. Add sulphuric acid to a little of the liquid.

8. Add hydrogen sulphide to a little of the liquid.

9. Pour ammonia on the filter, and wash out with water. Then add nitric acid to the filtrate.

What evidence do you get of the presence of silver and of mercury?

### STUDY OF GROUP II.

*Experiment 196.*—1. Prepare dilute solutions of copper sulphate, mercuric chloride, arsenic trioxide in hydrochloric acid, and of tin in hydrochloric acid. [Bismuth and antimony are omitted, as their presence gives rise to difficulties hard to deal with intelligently at this stage.] Add a little hydrochloric acid to the solutions of copper sulphate and of mercuric chloride.

2. Pass hydrogen sulphide through a small quantity of each of the solutions.

What takes place? What are the substances formed?

3. Filter and wash. Treat each precipitate with a solution of yellow ammonium sulphide.

What takes place? Add dilute sulphuric acid to the filtrates.

What takes place?

4. Treat the precipitates obtained from the copper and the mercury salts with concentrated warm nitric acid.

Does either one dissolve easily? What is the color of the solution?

5. Treat a little of the solution obtained in 4. with ammonia.

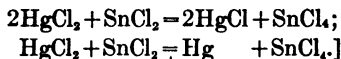
What is the result? How can you detect the presence of copper?

6. Treat with a mixture of nitric and hydrochloric acids the precipitate which is not readily dissolved by nitric acid alone. Evaporate the acid. Add water, and then a solution of tin in hydrochloric acid.

What is formed when tin is dissolved in hydrochloric acid?

What other compound of tin and chlorine is there?

[When stannous chloride,  $\text{SnCl}_2$ , acts upon mercuric chloride,  $\text{HgCl}_2$ , the former takes a part or all of the chlorine from the latter, forming either mercurous chloride,  $\text{HgCl}$ , or mercury, thus:



7. Treat the precipitate obtained in the case of the arsenic with 4-5 cc. of a concentrated solution of ammonium carbonate. To the solution add hydrochloric acid and a few crystals of potassium chlorate, and boil until chlorine is no longer given off. Add ammonia, ammonium chloride, and magnesium sulphate to the solution. [The precipitate is ammonium magnesium arsenate,  $\text{NH}_4\text{MgAsO}_4$ .]

8. Dissolve the tin precipitate in dilute hydrochloric acid. Add a few small pieces of zinc. Dissolve in hydrochloric acid the tin which separates.

What will the solution thus obtained contain?

What should take place on adding the solution to a solution of mercuric chloride? Try it.

Mix the solutions prepared in 1., and proceed as follows:

9. Pass hydrogen sulphide. Filter; wash. Treat the precipitate with ammonium sulphide. Filter; wash.

What is now in solution?

What is on the filter?

10. Treat the solution with dilute sulphuric acid. Filter; wash. Treat the precipitate thus obtained with concentrated ammonium carbonate. Filter; wash. Treat the solution as directed in 7., and the precipitate as in 8.

11. Treat with concentrated warm nitric and hydrochloric acids the precipitate left after treating with ammonium sulphide as in 9. Test for copper as in 5., and for mercury as in 6.

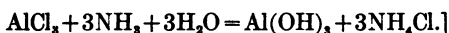
# STUDY OF GROUP III.

## ALUMINIUM.

*Experiment 197.*—1. Prepare a solution of ordinary alum.  
[What is ordinary alum?]

2. Add to this solution ammonia, ammonium chloride, and ammonium sulphide. Filter and wash. Treat the precipitate with hydrochloric acid; and then treat the solution thus obtained with ammonium chloride and ammonia.

[Aluminium does not form a sulphide; but the hydroxide,  $\text{Al}(\text{OH})_3$ , is formed when ammonia, ammonium chloride, and ammonium sulphide are added to a solution of its salts. When the hydroxide is treated with hydrochloric acid it is converted into the chloride,  $\text{AlCl}_3$ , which dissolves; and when the solution of the chloride is treated with ammonia the hydroxide is precipitated:



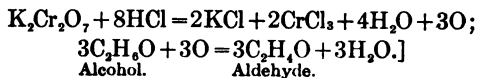
3. Dissolve the precipitate of aluminium hydroxide,  $\text{Al}(\text{OH})_3$ , in as little hydrochloric acid as possible, and add a cold solution of sodium hydroxide. Boil the solution thus obtained.

4. After cooling slowly add dilute hydrochloric acid. When the alkali is neutralized, aluminium hydroxide,  $\text{Al}(\text{OH})_3$ , will be precipitated. It will dissolve on the addition of more acid; and from the solution thus obtained the hydroxide can be precipitated by a solution of ammonia.

## CHROMIUM.

*Experiment 198.*—1. To 5–10 cc. of a solution of potassium dichromate in a test-tube add 10–15 drops of hydrochloric acid and 10–15 drops of alcohol, and boil. What change takes place?

[Under the conditions the chromium is changed to chromic chloride,  $\text{CrCl}_3$ , and the potassium to potassium chloride, while some of the oxygen of the dichromate acts upon the alcohol, converting it into aldehyde:



2. Treat the solution of chromic chloride,  $\text{CrCl}_3$ , obtained in 1. as directed in 2. and 3., Experiment 197, and note the differences. How could you distinguish between aluminium and chromium?

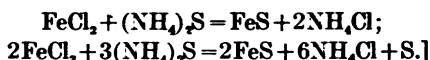
### IRON.

*Experiment 199.*—1. Prepare a solution containing ferrous chloride. [See Experiment 181.]

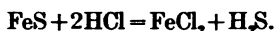
2. Convert a part of this into ferric chloride. [See Experiment 181.]

3. Treat each of these solutions with ammonia and ammonium sulphide.

[The same compound of iron is precipitated in both cases, and the action is represented thus:



4. Dissolve the precipitate in hydrochloric acid:



5. Convert the ferrous into ferric chloride. [See Experiment 181.]

6. Treat with ammonium chloride and ammonia.

What differences are there between aluminium, chromium, and iron?

7. Filter; dissolve the precipitate in hydrochloric acid; and treat with a solution of potassium ferrocyanide,  $\text{K}_4\text{Fe}(\text{CN})_6$ .

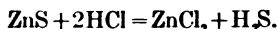
The precipitate formed in this case is Prussian blue.

### ZINC.

*Experiment 200.*—1. Prepare a dilute solution of zinc sulphate.

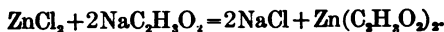
2. Treat with ammonia and ammonium sulphide. What is the color of the precipitate? The composition is  $\text{ZnS}$ .

3. Dissolve in dilute hydrochloric acid:



4. Treat with ammonium chloride and ammonia. Is a precipitate formed?

5. Add enough hydrochloric acid to give the solution an acid reaction, and then add sodium acetate,  $\text{NaC}_2\text{H}_3\text{O}_2$ :



6. Pass hydrogen sulphide through the solution. The white precipitate is zinc sulphide,  $\text{ZnS}$ .

What differences are there between aluminium, chromium, iron, and zinc? How could they be separated and detected if present in the same solution?

[It will be well for the instructor to prepare solutions containing two or more members of Group III, and to give them to the student for analysis.]

### MANGANESE.

*Experiment 201.*—1. Treat a little manganese dioxide in a test-tube with hydrochloric acid. Boil, dilute, and filter.

What have you in solution? [See page 112.]

2. Treat as under 2., 3., 4., 5., 6., in the preceding experiment. In what respects do manganese and zinc differ?

3. To the solution through which you have just passed hydrogen sulphide add sodium hydroxide,  $\text{NaOH}$ , until most of the acetic acid is neutralized; heat gently and add bromine-water. Let the liquid stand for an hour.

What takes place? [The composition of the precipitate is represented by the formula  $\text{Mn}(\text{OH})_2$ .]

How could you separate manganese from the other members of the group?

*Experiment 202.*—1. Mix dilute solutions of alum, chromic chloride (prepared as in Experiment 198, 1.), ferrous chloride (prepared as in Experiment 182), zinc sulphate, and manganous chloride.

2. Treat with ammonium chloride, ammonia, and ammonium sulphide. Filter and wash.

3. Treat the precipitate with dilute hydrochloric acid; treat

with nitric acid to convert ferrous chloride into ferric chloride (Experiment 181); and then treat the solution thus obtained with ammonium chloride and ammonia.

What have you in the precipitate? (Call this A.)

What in the solution? (Call this B.)

4. Dissolve the precipitate in a little dilute hydrochloric acid, and add a cold solution of sodium hydroxide, more than enough to neutralize the hydrochloric acid. Filter; dissolve the precipitate in hydrochloric acid; and treat with a solution of potassium ferrocyanide,  $K_4Fe(CN)_6$ . [See Experiment 199, 7.] Boil the filtrate from the precipitate of ferric hydroxide. What is precipitated? Treat the filtrate as directed in Experiment 197, 4.

5. Treat the solution B (see under 3., above), as directed under 5. and 6., Experiment 200; and under 3., Experiment 201. Examine mixtures containing members of Group III.

#### STUDY OF GROUP IV.

##### CALCIUM.

*Experiment 203.*—1. Prepare a solution of calcium chloride by dissolving a little calcium carbonate (marble) in hydrochloric acid. What is the reaction?

2. Treat with ammonium chloride, ammonia, and ammonium carbonate,  $(NH_4)_2CO_3$ . Filter and wash.

What takes place? Write the reaction.

3. Treat with potassium chromate. Is a precipitate formed?

4. Dissolve the precipitate in dilute hydrochloric acid. Treat a small part of this solution with a solution of calcium sulphate in water. Treat another small part with ammonia and ammonium oxalate,  $(NH_4)_2C_2O_4$ . The precipitate is calcium oxalate,  $CaC_2O_4$ . Does a solution of calcium chloride give a precipitate when treated with a solution of calcium sulphate?

##### BARIUM.

*Experiment 204.*—1. Prepare a dilute solution of barium chloride in water.

2. Treat as directed under 2., preceding experiment.

3. Dissolve the precipitate in dilute hydrochloric acid. Treat a small part of this solution with a solution of calcium sulphate in water. Treat another portion with ammonia and ammonium oxalate. The precipitate is barium oxalate.

4. Treat a portion of the barium chloride solution with potassium chromate. The yellow precipitate is barium chromate.

What differences do you notice between the conduct of calcium and that of barium?

In order to detect calcium in the presence of barium, precipitate the barium as chromate and test the filtrate for calcium by the ammonium carbonate test.

#### STRONTIUM.

*Experiment 205.*—1. Prepare a dilute solution of strontium nitrate in water.

2. Treat as directed under 2, 3, 4, Experiment 203.

Does a solution of strontium nitrate give a precipitate when treated with a solution of calcium sulphate?

What differences do you notice between the conduct of calcium, barium, and strontium?

In order to detect strontium in the presence of calcium and barium, precipitate the barium as chromate and test for the strontium with a solution of calcium sulphate.

Mix solutions of calcium, barium, and strontium salts and try the reactions described in Experiments 203, 204, and 205.

#### STUDY OF GROUP V.

##### MAGNESIUM.

*Experiment 206.*—1. Prepare a dilute solution of magnesium sulphate in water.

2. Add ammonium chloride, ammonia, and ammonium carbonate. Is a precipitate formed? Compare this reaction with that obtained in case of calcium, barium and strontium salts.

3. Add ammonium chloride, ammonia, and disodium phosphate. The precipitate is ammonium magnesium phosphate,  $\text{NH}_4\text{MgPO}_4$ .

What similar precipitate has already been obtained? (See Experiment 196, 7.)

4. Mix solutions of barium, calcium, strontium, and magnesium salts, and see whether you can detect the three metals by means of the reactions described in Experiments 203, 204, 205, and 206. It is necessary to remove calcium, barium and strontium before testing for magnesium.

#### STUDY OF GROUP VI.

*Experiment 207.*—1. Potassium can be detected by means of the color it gives to a flame (see Experiment 150); and also by the fact that when chlorplatinic acid,  $H_2PtCl_6$ , is added to a solution of a potassium salt, the salt,  $K_2PtCl_6$ , is precipitated. Try this.

2. Sodium is detected by means of the flame reaction (see Experiment 150).

3. Ammonium salts are detected by adding an alkali, when ammonia gas is given off, and this is easily recognized.

**General Directions.**—By the aid of the reactions thus far studied it will be found possible to analyze substances containing the following metals either alone or mixed together: Silver, lead, mercury, copper, tin, arsenic, aluminium, chromium, iron, zinc, manganese, calcium, barium, magnesium, potassium, sodium, and ammonium. After the metals have been detected, the next question to be answered is: In what forms of combination were they present in the original substance taken for analysis? Or, in other words, what salts were present? To answer this question, recall the experiments you have made in the general reactions of chlorides, nitrates, sulphates, and carbonates. These are the most common salts and, for the present, it will be best to confine your work to these.



**Classification of Substances Studied.**—It will now be well to draw up a table containing the names and symbols of all the substances with which you have had to deal, classifying them into:

- (1) *Elements* and *Compounds*;
- (2) *Acids*, *Bases*, and *Salts*.

Under *Elements* state the principal source and the principal method of getting each.

Under *Compounds* state the source and the principal method of preparation of each.

Classify all the compounds you have had to deal with into:

- (1) Those which are gaseous;
- (2) Those which are liquid;
- (3) Those which are solid at the ordinary temperature;
- (4) Those solids and liquids which easily undergo change when heated (state what the change is, and give the equation expressing the change).

Classify the compounds further into:

- (1) Those which are soluble in water;
- (2) Those which are insoluble in water.

## APPENDIX I.

### MEASUREMENT OF GASES.

THE volume of a gas is changed by a change in temperature and a change in the pressure. Therefore in measuring the volume of a gas corrections must be made. The principles involved are presented in the following paragraphs:

**Law of Dalton and Gay Lussac—Correction for Temperature.**—When the temperature of a gas is raised one degree Centigrade its volume is increased  $\frac{1}{273}$  part of the volume occupied by it at  $0^{\circ}$ . If, therefore, the volume of a gas at  $0^{\circ}$  is  $V$ , at  $t^{\circ}$  its volume  $v$  will be

$$V + \frac{t}{273} \cdot V, \text{ or } v = V + \frac{t}{273} \cdot V.$$

This expression may also be written

$$v = V + 0.00366t \times V, \text{ or } v = V(1 + 0.00366t).$$

From this it follows that

$$V = \frac{v}{1 + 0.00366t}.$$

This is called the law of Dalton and Gay Lussac as it was discovered by them simultaneously in 1801. It is also sometimes called the law of Charles for the reason that this physi-

cist discovered it in 1787, though he stated it in a somewhat different form.

It is customary to reduce the observed volume of a gas to the volume which it would have at  $0^{\circ}$ . The correction is made in accordance with the above expression. Thus, if the volume of a gas is found to be 250 cubic centimetres at  $15^{\circ}$ , and it is required to find what its volume would be at  $0^{\circ}$ , the calculation is made as follows: In this case  $v$ , the observed volume, is 250 cc.;  $t$ , the temperature, is  $15^{\circ}$ . Substituting these values in the equation

$$V = \frac{v}{1 + 0.00366t}$$

we have

$$V = \frac{250}{1 + 0.00366 \times 15}$$

from which we get 236.99 as the value of  $V$ .

**Boyle's Law.**—But the volume of a gas varies also according to the pressure. When the pressure is doubled the volume is decreased to one half; and when the pressure is decreased to one half, the volume is doubled, and so on. In other words, the volume of a gas is inversely proportional to the pressure. Increase the pressure two, three, or four times and the volume becomes one half, one third, or one fourth, and *vice versa*. If the gas has the volume  $V$  at the pressure  $P$ , and at pressure  $p$  the volume  $v$ , these values bear to one another the relations expressed as follows:

$$v:V::P:p,$$

or

$$PV = pv.$$

This law was discovered by Boyle in 1660 and is called *Boyle's law*.

**Correction for Pressure.**—The pressure is usually stated in millimetres, and reference is to the height of a column of mercury to which the pressure corresponds. A gas contained in an open vessel, or in a vessel over mercury or water, in which the level of the liquid inside and outside the vessel is the same, is under the pressure of the atmosphere. What that is we learn from the barometer. As this pressure varies, it is necessary to read the barometer whenever a gas is measured, and then to reduce the observed volume to certain conditions which are accepted as standard. When the gas is measured in a tube over mercury or water, and the level of the liquid inside the tube is higher than that outside, the gas is under diminished pressure, the amount of diminution depending on the height of the column of mercury or water in the tube. Thus, if the arrangement is as represented in Fig. 56, and the height of the mercury column above

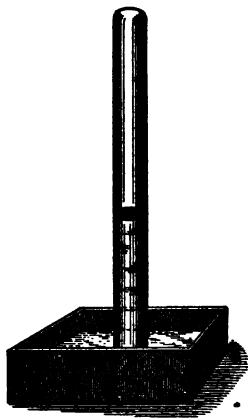


FIG. 56.

the level of the mercury in the trough is 100 millimetres, and the pressure of the atmosphere is 760 millimetres, then the gas in the tube is not under the full atmospheric pressure, for the atmospheric pressure exerted on the mercury is supporting a column of mercury 100 millimetres high, and the pressure actually brought to bear on the gas corresponds to  $760 - 100 = 660$  mm. Suppose that

in this case the volume of gas actually measured is 75 cc. Call this  $v$ . What would be the actual volume  $V$  of the gas under the standard pressure 760 mm.? We have seen that

$$PV = pv.$$

Now  $P = 760$ ,  $v = 75$ , and  $p = 660$ . Therefore,

$$760 V = 75 \times 660, \text{ or } V = \frac{75 \times 660}{760} = 65.13.$$

**Combined Volumetric Corrections.**—In all cases it is necessary to make the above corrections in dealing with the volumes of gases. The correction for temperature and that for pressure may be made in one operation, the formula being

$$V = \frac{vp}{760(1 + 0.00366t)},$$

in which  $V$  = the volume of the gas at  $0^\circ$  and 760 mm. pressure;  $v$  = the observed volume;  $t$  = the observed temperature;  $p$  = the pressure under which the gas is measured.

**Corrections for Aqueous Pressure.**—The pressure of water-vapor in a gas also influences its volume, and this must be taken into account. The formula for making all the corrections required in determining the volume of a gas is

$$V = \frac{v(p - a)}{760(1 + 0.00366t)},$$

in which  $a$  is the pressure of water-vapor at  $t^\circ$ .

[PROBLEMS.—The volume of a gas contained in a eudiometer measures 42 cc. The height of the mercury column over which it stands is 68 mm. The barometer indicates an atmospheric

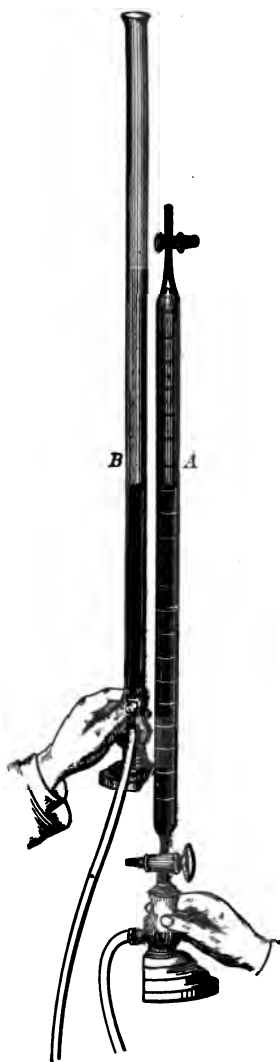


FIG. 57.

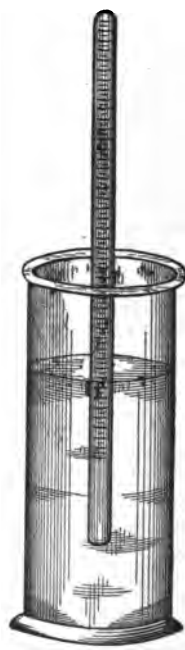


FIG. 58.

pressure of 746 mm. The temperature is  $18^{\circ}\text{C}$ . What would be the volume of the gas at  $0^{\circ}$  and 760 mm. pressure?

The volume of a gas contained in a vessel over a column of mercury 85 mm. high measures 24 cc. The barometer indicates a pressure of 774 mm. The temperature is  $19^{\circ}$ . What would be the volume of the gas under normal conditions, *i.e.*,  $t=0^{\circ}$  and  $P=760$  mm.?

The volume of a gas contained in a vessel over water, the level of the water inside and outside being the same:  $v=80$  cc.;  $t=20^{\circ}$ ;  $p=740$  mm.;  $a=17.4$  at  $20^{\circ}$ . What is the value of  $V$  or the volume at  $0^{\circ}$  and 760 mm.?

**Apparatus for Measuring the Volume of a Gas.**—A convenient apparatus for measuring gas-volumes is that represented in Fig. 57. It consists of two tubes connected at the base by means of a piece of rubber tubing and containing water. The tube *A* is graduated, the other is not. The gas to be measured is brought into the tube *A*, and the other tube is then placed at the side of the one containing the gas, and its height adjusted so that the column of liquid in both tubes is at the same level. Under these circumstances, obviously the gas is under the atmospheric pressure for which the necessary correction must, of course, be made. It is also necessary in this case to make the corrections for temperature and for the pressure of water-vapor. It is, further, sometimes convenient when the gas is measured over water to transfer the measuring-tube to a vessel containing enough water to permit the immersion of the tube to a point at which the level of the liquid inside and outside the tube is the same. In this case the conditions are the same as in the apparatus just described. The arrangement is shown in Fig. 58.

## APPENDIX II.

### FILTERING AND WASHING.

**Directions for Making a Wash-bottle.**—A 750-cc. Florence flask is generally used for this purpose. If a two-hole rubber stopper is not available, select a cork stopper which will fit the flask tightly, and soften it by rolling with a board or the foot. In boring the two holes for the glass tubes always use a cork-borer which is no larger than the tubing, and bore from both ends in order to avoid breaking the cork. If the holes are cut by turning the cork-borer while exerting a slight pressure upon it, the sides of the holes will be smooth. Now bend two pieces of glass as shown in Fig. 59, being careful to make the acute angle of one and the obtuse angle of the other such that the mouthpiece and the nozzle will form a straight line. The bends should not be more than one and a half inches above the stopper, and the mouthpiece and nozzle should not be more than three and four inches long respectively. In bending glass use only the fish-tail burner, and after the glass begins to get hot hold it perfectly straight and allow the weight of the glass beyond the heated portion to produce the bend. By removing the

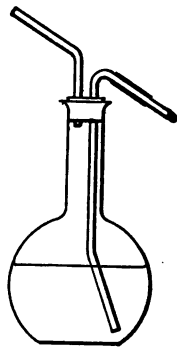


FIG. 59.



glass from the flame and holding it so that the bent part is perpendicular, the bending may be stopped at any point. Always round off the sharp edges of the tubing by holding the ends in the Bunsen flame and turning until the glass has softened and become smooth. The short tip to the nozzle can be prepared by heating a piece of tubing in the Bunsen flame, turning constantly, until it becomes soft and then removing it from the flame and pulling it out to a small capillary. The capillary is then cut off and the tip joined to the nozzle by a short piece of rubber tubing.

**Directions for Filtering.**—A precipitate can be separated from the liquid in which it is suspended by passing the liquid through a filter of unsized paper, the pores of which are too fine to permit the passage of the solid substance. The filter-paper should never project above the top of the funnel. The round paper should be folded in half and in quarter and opened with three thicknesses of paper on one side and one on the other as shown in Fig. 60. The filter should be pushed down until it fits close against the funnel and moistened to keep it in position. To wash a precipitate pour water over it and allow the liquid to run through, in that way extracting all the soluble material from the precipitate. This process is more rapid and complete if each portion is allowed to run out before any more is added. At the end wash all the precipitate from the sides of the filter down into the tip by means of a stream from the wash-bottle.



FIG. 60.

## APPARATUS AND CHEMICALS.

A FEW of the experiments described in this book are not suitable for general laboratory practice; they are intended for the lecture-room and require a trained experimenter to secure the best results. Others again, although easily performed by any student, yet on account of the character of the apparatus required—its cost or its bulkiness—may have to be omitted from the laboratory course after they have been performed in the lecture-room. To these two classes the following may be considered as belonging: Nos. 4, 25, 26, 27 (with reference to potassium), 28, 34, 43,, 45, 47, 48, 55, 117.

As regards the apparatus called for, the following may be said: To secure the best results it will be well to follow the form described. Changes will sometimes be advisable to meet special conditions. For example, on account of the difficulty of obtaining large corks free from perforations and therefore suitable for wash-cylinders, an excellent substitute will be found in a wide U-tube, in which the wash-liquid—sulphuric acid, water, potassium permanganate solution, etc.—acts as a “trap,” merely closing the bend. When the quantity of gas to be purified is not great, this device gives good results.

Again, if it is necessary still further to reduce the cost of the apparatus to be used, passable results can be obtained by the use of wide test-tubes, in the place of flasks, in such

experiments as Nos. 16, 49, 70, 91, 92, 93, 112, 114. Of course the quantities of materials used would in such cases be greatly decreased.

As a rule, it is better, whenever a solid substance is to be heated to a high temperature, to use a tube of hard glass. An ordinary arsenic-tube, or matrass, serves very well.

For the benefit of those who have no laboratory at command, and who may wish to make arrangements for going through with the experimental work, the following lists have been drawn up. In them are included everything necessary to perform the experiments on a small scale. Should it be desired to fit up a room with conveniences for students, the amount of apparatus necessary would depend upon the number of students, but for each individual the expense would be small, as many of the pieces of apparatus, such as are included in List II, need not be multiplied. In place of some of the pieces of apparatus described in the book, ordinary kitchen utensils will answer: thus, for example, instead of the trough for collecting gases, a tin pan or a deep earthenware dish may be used; instead of the water-bath, a stew-pan, fitted with two or three tin or sheet-iron rings of different sizes; and in the place of glass cylinders for working with gases, wide-mouthed cheap bottles.

With regard to the chemicals the same thing may be said: Some of those on the list are provided for in quantity sufficient for several students. The amounts in such cases are as small as can generally be obtained from dealers.

To summarize: List I comprises such apparatus as will probably be needed for each student; List II, such apparatus as will serve without duplication for a small class; List III, the chemicals actually needed for each student, as nearly as can be calculated under the circumstances.

## LIST I.—APPARATUS.

Arsenic-tubes, 6.....	\$0 30	Iron pan (5 in.).....	\$0 20
Beakers, nest (100-700 cc.)....	90	" stand, with clamp.....	90
Blowpipe.....	14	Mortar, porcelain (100 mm.)....	50
Bunsen Burner.....	45	Retorts, 3 (1, 60 cc.; 1, 100; 1,	
Combustion-tubing, 1 ft.....	18	250, tubulated).....	75
Corks, 2 dozen, assorted.....	25	Rubber tubing, 2 ft. for burner..	39
Crucibles, porcelain, 2(35-40 mm.)	37	"          2 ft. for connec-	
Deflagrating-spoon.....	25	tions.....	23
Evaporating-dishes, 2 (75-100		Safety-tube.....	23
mm.).....	48	Test-tubes, 12 (6, 6× $\frac{1}{2}$ in.; 6,	
File, round.....	20	6× $\frac{1}{2}$ in.).....	35
triangular.....	20	Test-tube Stand.....	25
Filter-paper, 1 quire.....	35	Thistle-tube.....	12
Flasks, Florence, 4 (1, 50 cc.; 1, 100		Tripod.....	30
cc.; 1, 250; 1, 500; 1, 750)....	71	U tubes, 2 (4× $\frac{1}{2}$ in.).....	28
Flasks, Wolff, 1 (300 cc.).....	45	Watch-glasses, 2 (50 mm.).....	10
Funnels 2 (1, 50 mm.; 1, 90 mm.)	30	Wire: 1 ft. magnesium; 6 in.	
Gauche, wire, 6×6 in.....	15	platinum.....	35
Glass tubing, soft, $\frac{1}{8}$ lb.....	10		
rod, 1 oz.....	10		\$10 77

## LIST II.

Burette, Mohr, graduated to $\frac{1}{10}$		Measuring-glass, 4 oz. (10 p. c.)	\$0 30
cc., 50 cc. complete (20 p. c.)	\$1 50	Pinch-cock, Hoffman, medium	
Cells, Bunsen, 2 Quarts (10 p. c.)	2 20	(20 p. c.).....	25
Cork-borers, set (6).....	1 00	Scales, set (20 p. c.).....	85
Condenser and tubing (20 p. c.)	1 85	Weights, set (20 p. c.).....	75
Gas-measuring tube, graduated to			
$\frac{1}{8}$ cc., 25 cc. (20 p. c.).....	1 00		\$10 10
Magnet, 6-in. horseshoe.....	40		

## LIST III.—CHEMICALS.

Acid, Hydrochloric (conc.) $\frac{1}{2}$ lb.		Copper Oxide, 2 oz.....	\$0 10
(bottle 12 cents extra).....	\$0 10	Sulphate, $\frac{1}{2}$ lb.....	10
Acid, Nitric (conc.), $\frac{1}{2}$ lb. (bottle		Ferric Chloride, 1 oz.....	10
12 cents extra).....	10	Ferrous Sulphate, 2 oz.....	10
Acid, Oxalic, 1 oz.....	10	Sulphide, $\frac{1}{2}$ lb.....	10
Sulohuric (conc.), 2 lbs.		Gall-nuts, 1 oz.....	10
(bottle 15 cents extra).....	10	Glucose, 5 oz.....	10
Alcohol, 8 oz. (bottle 8 cents ex-		Gypsum (crystallized), $\frac{1}{2}$ lb.....	10
tra).....	20	Iodine, $\frac{1}{2}$ oz. (bottle 5 cents extra)	15
Alum, 2 oz.....	10	Iron Filings, 2 oz.....	10
Ammonia (conc.), $\frac{1}{2}$ lb. (bottle 12		Lead (granulated), 2 oz.....	10
cents extra).....	10	Nitrate, 2 oz.....	10
Ammonium Carbonate, 2 oz. (bot-		Oxide, 1 oz.....	10
tle 4 cents extra).....	10	Peroxide, 1 oz.....	10
Chloride, $\frac{1}{2}$ lb.....	10	Litmus, 1 oz.....	10
Nitrate, 1 oz.....	10	Paper, red and blue, 1	
Antimony, 1 oz.....	10	sheet each.....	10
Arsenic Trioxide, 2 oz.....	10	Magnesium Sulphate, 1 oz.....	10
Barium Chloride, 2 oz.....	10	Manganese Dioxide, $\frac{1}{2}$ lb.....	10
Bismuth, $\frac{1}{2}$ oz.....	10	Mercuric Oxide, 1 oz.....	15
Bone-black, 1 oz.....	10	Mercury, 2 oz. (bottle 3 cents	
Borax, 1 oz.....	10	extra).....	10
Calcium Chloride, $\frac{1}{2}$ lb. (bottle 8		Minium, 1 oz.....	10
cents extra).....	10	Phosphorus, 1 oz. (bottle 5 cents	
Fluoride, 1 oz.....	10	extra).....	15
Carbon Bisulphide 4 oz. (bottle 4		Potassium Bromide, 1 oz.....	10
cents extra).....	10	Carbonate, $\frac{1}{2}$ lb.....	10
Copper shavings, $\frac{1}{2}$ lb.....	20	Chlorate, $\frac{1}{2}$ lb.....	10

Potassium Chromate, 2 oz. ....	10	Sodium, Hydroxide, $\frac{1}{2}$ lb. (bottle	
" Dichromate, $\frac{1}{2}$ lb. ....	10	5 cents extra). ....	15
" Ferrocyanide, 1 oz. ....	10	" Nitrate, 2 oz. ....	10
" Hydroxide, 6 oz. (bot-		" Phosphate, 2 oz. ....	10
tle 6 cents extra). ....	20	" Sulphate, $\frac{1}{2}$ lb. ....	10
" Iodide, 1 oz. (bottle 3		Strontium Nitrate, 1 oz. ....	10
cents extra). ....	25	Sulphur, roll, $\frac{1}{2}$ lb. ....	10
" Nitrate, 2 oz. ....	10	Tartar Emetic, 1 oz. ....	10
" Permanganate, 2 oz. ....	10	Tin, granulated, $\frac{1}{2}$ lb. ....	10
Sodium, 1 dram (bottle 4 cents		Zinc, granulated, 1 lb. ....	20
extra). ....	10	" Sulphate, 1 oz. ....	10
" Carbonate, 2 oz. ....	10		
" Chloride, 1 lb. ....	10		\$7 25

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# LIST OF THE ELEMENTS, THEIR SYMBOLS AND ATOMIC WEIGHTS.

	H=1	O=16		H=1	O=16
Aluminium	Al.. 26.9	27.1	Molybdenum	Mo. 95.2	96.0
Antimony	Sb..119.2	120.2	Neodymium	Nd..143.2	144.3
Argon	A.. 39.6	39.9	Neon	Ne.. 19.8	20.0
Arsenic	As.. 74.4	75.0	Nickel	Ni.. 58.21	58.68
Barium	Ba..136.28	137.37	Nitrogen	N.. 13.90	14.01
Bismuth	Bi..206.3	208.0	Osmium	Os..189.4	190.9
Boron	B.. 10.9	11.0	Oxygen	O.. 15.87	16.00
Bromine	Br.. 79.28	79.92	Palladium	Pd..105.8	106.7
Cadmium	Cd..111.51	112.40	Phosphorus	P.. 30.8	31.0
Caesium	Cs..131.75	132.81	Platinum	Pt..193.5	195.0
Calcium	Ca. 39.77	40.09	Potassium	K.. 38.79	39.10
Carbon	C.. 11.90	12.00	Praseodymium	Pr..138.5	140.6
Cerium	Ce..139.14	140.25	Radium	Ra..226.6	226.4
Chlorine	Cl.. 35.18	35.46	Rhodium	Rh..102.1	102.9
Chromium	Cr. 51.7	52.1	Rubidium	Rb. 84.77	85.45
Cobalt	Co. 58.50	58.97	Ruthenium	Ru..100.9	101.7
Columbium	Cb. 92.8	93.5	Samarium	Sa..149.1	150.4
Copper	Cu. 63.07	63.57	Scandium	Sc.. 43.8	44.1
Dysprosium	Dy..161.2	162.5	Selenium	Se.. 78.6	79.2
Erbium	Er..166.0	167.4	Silicon	Si.. 28.1	28.3
Europium	Eu..150.8	152.0	Silver	Ag..107.02	107.88
Fluorine	F.. 18.8	19.0	Sodium	Na.. 22.82	23.00
Gadolinium	Gd..156.1	157.3	Strontium	Sr.. 86.92	87.62
Gallium	Ga.. 69.3	69.9	Sulphur	S.. 31.82	32.07
Germanium	Ge.. 71.9	72.5	Tantalum	Ta..179.6	181.0
Glucinum	Gl. 9.0	9.1	Tellurium	Te..126.5	127.5
Gold	Au..195.6	197.2	Terbium	Tb..157.9	159.2
Helium	He. 4.0	4.0	Thallium	Tl..202.4	204.0
Hydrogen	H.. 1.00	1.01	Thorium	Th..230.58	232.42
Indium	In..113.9	114.8	Thulium	Tm..167.2	168.5
Iodine	I..125.91	126.92	Tin	Sn..118.1	119.0
Iridium	Ir..191.6	193.1	Titanium	Ti.. 47.7	48.1
Iron	Fe. 55.41	55.85	Tungsten	W..182.5	184.0
Krypton	Kr. 81.1	81.8	Uranium	U..236.6	238.5
Lanthanum	La..137.9	139.0	Vanadium	V.. 50.8	51.2
Lead	Pb..205.46	207.10	Xenon	Xe..127.0	128.0
Lithium	Li. 6.94	7.00	Ytterbium		
Lutecium	Lu..172.6	174.0	(Neoytterbium)	Yb..170.6	172.0
Magnesium	Mg. 24.13	24.32	Yttrium	Y.. 88.3	89.0
Manganese	Mn. 54.49	54.93	Zinc	Zn.. 64.85	65.37
Mercury	Hg..198.4	200.0	Zirconium	Zr. 89.9	90.6